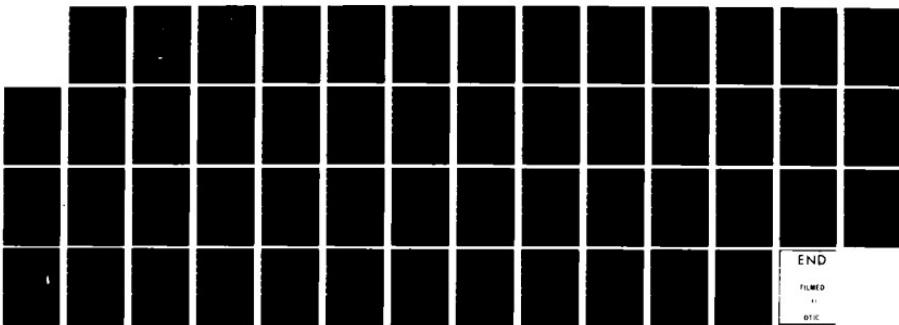
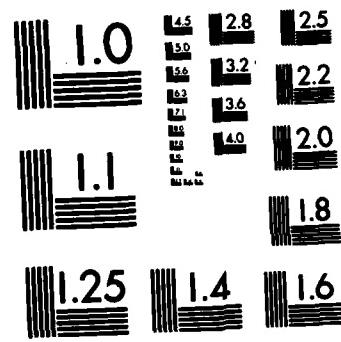


AD-A125 252 SYNTHESIS OF CIS- AND
TRANS-1357-TETRANITRO-1357-TETRAAZADECALIN TWO NEW
ENERGETIC MATERIALS(U) NAVAL WEAPONS CENTER CHINA LAKE
UNCLASSIFIED CA R L WILLER JAN 83 NWC-TP-6416 F/G 19/1 NL

1/1



END
FILMED
11
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

NWC TP 6416

12

Synthesis of *Cis*- and *Trans*- 1,3,5,7-Tetranitro-1,3,5,7- Tetraazadecalin, Two New Energetic Materials

AD A125232
1M

by
Rodney L. Willer
Research Department

JANUARY 1983

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555



Approved for public release; distribution unlimited.

DNC FILE COPY

83 03 03 025

A

Naval Weapons Center

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

FOREWORD

The Navy has a need for new energetic compounds which are both dense and energetic and which also have high thermal stability and low sensitivity to impact. These compounds could be used as ingredients in new propellant and explosive formulations which would simultaneously optimize both the performance and safety of new weapons systems. This report describes the synthesis and preliminary characterization of two such compounds, *cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin and *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin.

The work was performed under NAVSEA Project No. SR02402, under sponsorship of H. G. Adolph, Naval Surface Weapons Center (R-11).

The work was reviewed for technical accuracy by R. L. Atkins and A. T. Nielsen.

Approved by
E. B. Royce, Head
Research Department
28 December 1982

Under authority of
J. J. LAHR
CAPT. U.S. NAVY
Commander

Released for publication by
B. W. HAYS
Technical Director

NWC Technical Publication 6416

Published by.....Technical Information Department
Collation.....Cover, 25 leaves
First Printing.....140 unnumbered copies

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC TP 6416	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SYNTHESIS OF CIS- AND TRANS-1,3,5,7-TETRANITRO- 1,3,5,7-TETRAAZADECALIN, TWO NEW ENERGETIC MATERIALS		5. TYPE OF REPORT & PERIOD COVERED Interim - Feb 1982-Dec 1982
7. AUTHOR(s) Rodney L. Willer		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE-61153N, Project-SR02402, Task Area-SR02402, Work Unit Number-138509
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Center China Lake, CA 93555		12. REPORT DATE January 1983
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		13. NUMBER OF PAGES UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polynitramines High Energy Compounds High Density Compounds		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See back of form.		

~~UNCLASSIFIED~~
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(U) *Synthesis of Cis- and Trans-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin, Two New Energetic Materials*, by Rodney L. Willer, China Lake, Calif., Naval Weapons Center, January 1983. 50 pp. (NWC TP 6416, publication UNCLASSIFIED.)

(U) The synthesis and preliminary characterization of two new energetic materials, *cis-* and *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin are described.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or Special	

A handwritten signature or mark is visible at the bottom left of the form.

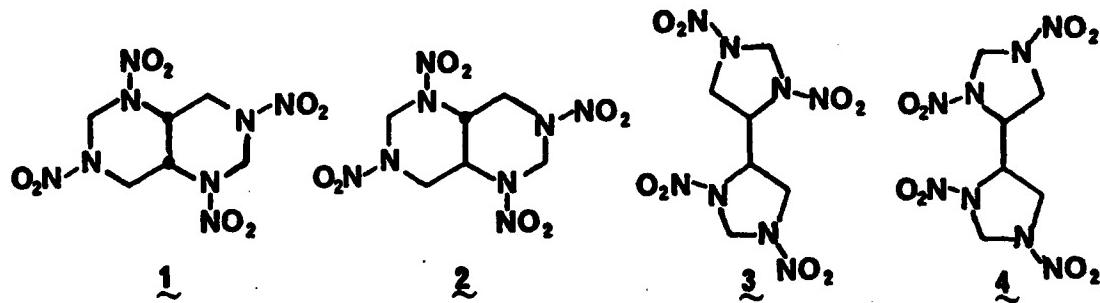
~~UNCLASSIFIED~~
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CONTENTS

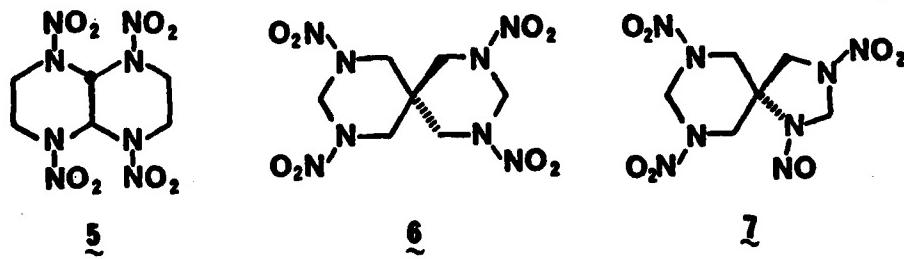
Introduction	3
Results	6
Synthesis	6
<i>Cis</i> -1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1)	6
<i>Trans</i> -1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (2)	8
Physical and Chemical Properties of 1, 2, 3, and 4	9
Discussion	10
Synthesis	10
Physical and Chemical Properties	11
Melting Points	11
Densities	12
Impact Sensitivities	13
Heats of Formation	13
Experimental	14
Diethyl-2,3-O-cyclohexylidine-L-tartrate (16)	14
L-threitol (14)	14
L-threitol-tetrabenzenesulfonate (18)	15
<i>Threo</i> -1,2,3,4-tetraazidobutane (19)	16
<i>Threo</i> -1,2,3,4-tetraaminobutane (10)	16
<i>Cis</i> -1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (8) and <i>D</i> -(4,4')-bi-(1,3-dinitroso-1,3-diazacyclopentane) (22)	16
<i>Cis</i> -1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1) and <i>D</i> -4,4'-(1,3-dinitro-1,3-diazacyclopentane) (3)	17
Separation of 1 and 3	17
<i>Meso</i> -erythritol Tetrabenzenesulfonate (23)	18
<i>Erythro</i> -1,2,3,4-tetraazidobutane (24)	18
<i>Meso</i> -1,2,3,4-tetraaminobutane (13)	19
<i>Trans</i> -1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (11)	19
<i>Trans</i> -1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (2)	19
<i>Meso</i> -4,4'-(1,3-dinitro-1,3-diazacyclopentane) (4)	20
Appendices:	
A. Infrared Spectra of Compounds	21
B. ¹ H NMR Spectra of Compounds	31

INTRODUCTION

This paper describes the synthesis and preliminary characterization of two new tetranitramino compounds, *cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin, 1, and *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin, 2. Also isolated and partially characterized were two by-products of the synthesis of 1 and 2, *d,l*-4,4'-bi-(1,3-dinitro-1,3-diazacyclopentane), 3, and *meso*-4,4'-bi-(1,3-dinitro-1,3-diazacyclopentane), 4. This work is a continuation of our work on developing new methodology for the



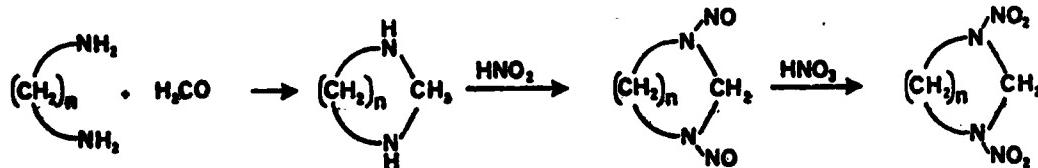
synthesis of polynitramino compounds and establishing the effect of stereochemistry and isomerization on the physical and chemical properties of polynitramino compounds.



Our previous work in this area has resulted in the synthesis of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin, λ ,¹ 2,4,8,10-tetranitro-2,4,8,10-tetraazaspiro[5.5]undecane, μ ,² and an improved synthesis of 1,3,7,9-tetranitro-1,3,7,9-tetraazaspiro[4.5]decane, λ .³ Compounds λ and μ are isomeric (i.e., both C₆H₁₀N₈O₈) yet they have very different densities (1.80 g/cc for λ^1 and 1.70 g/cc for λ^3). This large difference in densities for λ and μ prompted us to formulate other structures which are isomeric with λ and μ . Two such compounds were λ and μ . We felt that these compounds were very attractive synthetic targets because they retained the basic decalin ring structure of λ but moved the nitramino substituents around the ring. This would allow us to determine the effects of placement of the nitramino further away from each other. Since we hoped to be able to synthesize both stereo isomers (*cis*- and *trans*-), we could determine the effect of the stereochemistry at the ring junction on the density of these polynitramino compounds.

Our strategy for the synthesis of λ and μ was based on our previously developed methodology for the synthesis of polynitramino compounds. This technique involves the trapping of an *in situ* generated 1,3-diazacycloalkane with nitrous acid to give a 1,3-dinitroso-1,3-diazacycloalkane followed by nitrolysis of the dinitroso compound to the corresponding 1,3-dinitro-1,3-diazacycloalkane with 100% nitric acid (see Scheme 1).² A retro-synthetic analysis of λ and μ based upon

SCHEME 1. Synthetic Methodology for 1,3-Dinitro-1,3-diazacycloalkanes.



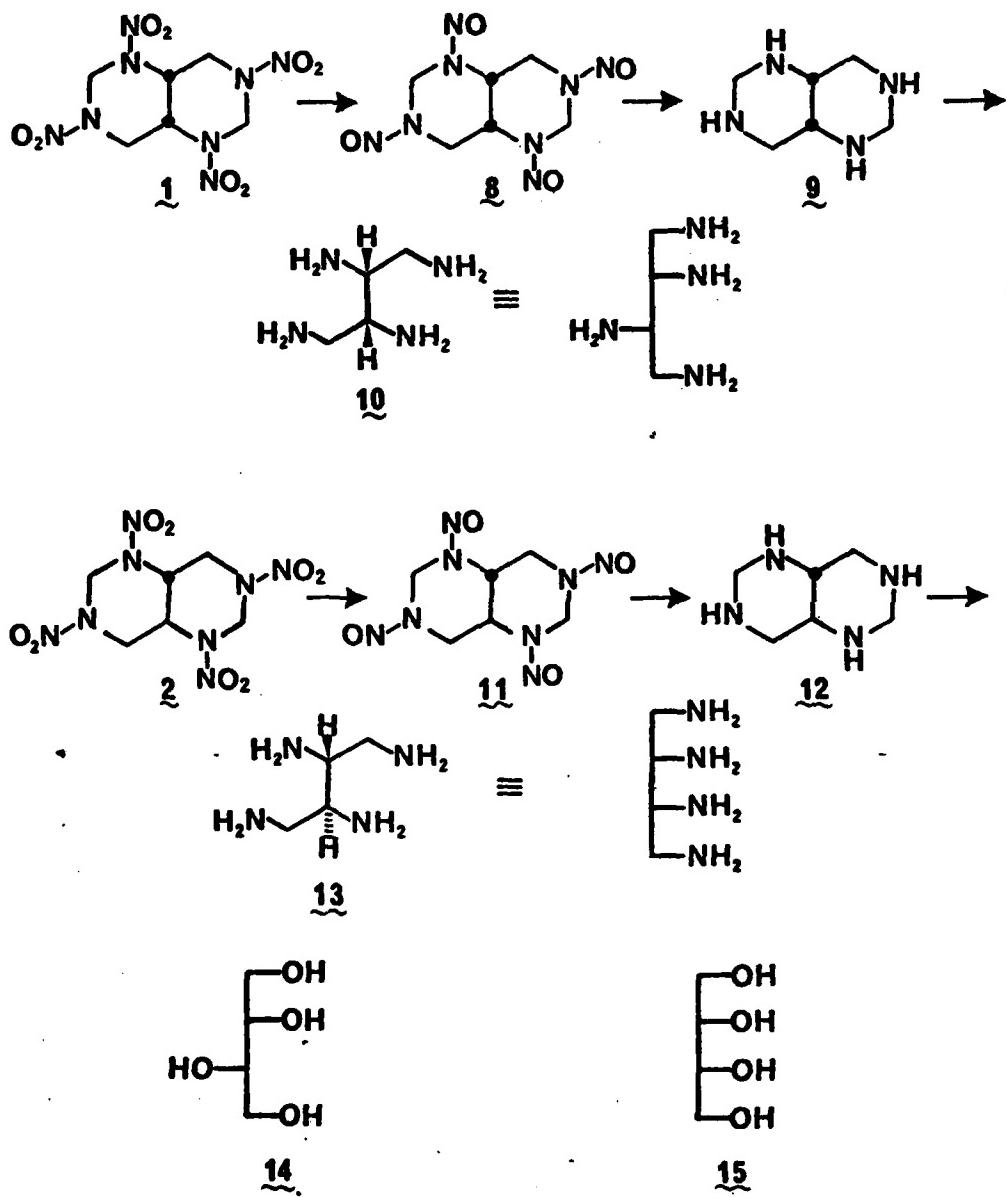
¹ Naval Weapons Center. *Synthesis of a New Explosive Compound, Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin*, by R. L. Willer, China Lake, Calif., NWC, August 1981. 16 pp. (NWC TP 6303, publication UNCLASSIFIED.)

² -----. *Synthesis and Characterization of a New Insensitive High Energy Polynitramino Compound, 2,4,8,10-Tetranitro-2,4,8,10-tetraazaspiro-[5.5]undecane (TNSU)*, by R. L. Willer, China Lake, Calif., NWC, March 1982. 10 pp. (NWC TP 6353, publication UNCLASSIFIED.)

³ -----. *Synthesis and Characterization of 1,3,5,7-Tetranitro-1,3,5,7-tetraazaspiro[4.5]decane (TNSD)*, by R. L. Willer, China Lake, Calif., NWC, January 1982. 10 pp. (NWC TM 4703, publication UNCLASSIFIED.)

this synthetic methodology indicated (see Scheme 2) that the required starting materials were *threo*-1,2,3,4-tetraaminobutane, 10, for 1 and *erythro*-1,2,3,4-tetraaminobutane, 13, for 2. Our strategy for the synthesis of the unknown 10 and 13 was to start with the corresponding tetrahydroxybutanes (*threitol*, 14, and *erythritol*, 15). These would be

SCHEME 2. Retro-Synthetic Analysis of 1 and 2.



converted to the amines by standard procedures^{2,4a,4b} of converting them first to their tetrabenzenesulfonate derivatives using benzenesulfonyl chloride in pyridine, then converting the tetrabenzenesulfonates to the tetraazides using sodium azide in dimethyl formamide (DMF), and finally reduction of the tetraazide to the tetraamine by catalytic hydrogenation.

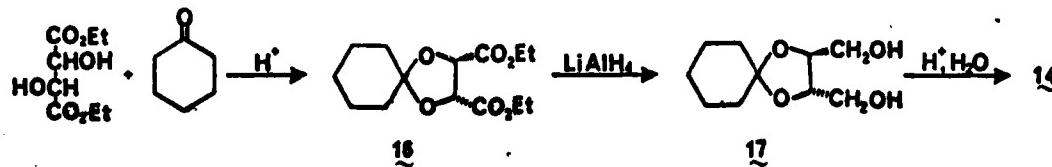
RESULTS

SYNTHESIS

Cis-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1)

The starting material, threitol (14), is commercially available, but quite expensive. We, therefore, chose to synthesize it from diethyl-L-tartrate using the procedure summarized in Scheme 3. This synthesis was adapted from one developed by R. U. Lemieux and J. Howard.⁵ Several minor modifications to the published procedures were made which both increased yields and simplified the procedures. These are detailed in the experimental section. An attempted direct reduction of diethyl-L-tartrate to L-threitol with LiAlH₄ failed.

SCHEME 3. Synthesis of L-threitol.



The conversion of the L-threitol to *threo*-1,2,3,4-tetraaminobutane, 10, is summarized in Scheme 4. The L-threitol was converted to its tetrabenzenesulfonyl derivative, 18, in 70% yield using standard methodology. The tetrabenzenesulfonate was then converted to the tetraazide,

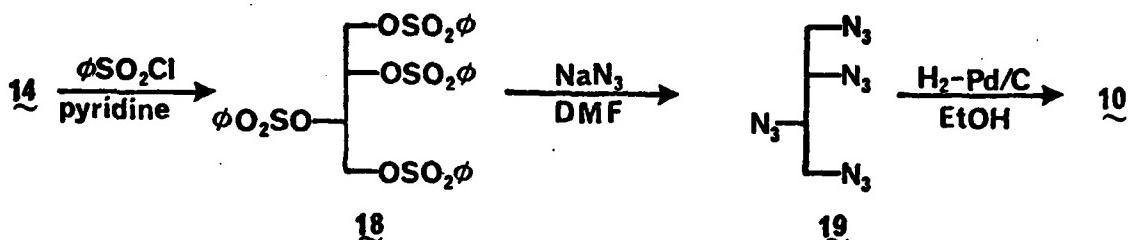
^{4a} E. B. Fleischer, et al. "Conversion of Aromatic and Alicyclic Polyalcohols to the Corresponding Primary Polyamines," *J. Org. Chem.*, Vol. 36 (1971), p. 3042.

^{4b} P. Anselme. "Catalytic Reduction of 1,1,1-Tris/azidomethylmethane to 1,1,1-Tris/aminemethylmethane," *Org. Prep. and Procedures*, Vol. 6 (1974), p. 103.

⁵ R. U. Lemieux and J. Howard. "The O-Inside Conformation of 1,3:2,4-Di-O-Methylene-L-Threitol," *Can. J. Chem.*, Vol. 41 (1963), p. 393.

19 , using sodium azide in DMF at 100°C . The crude azide, 19 , was then reduced to the *threo*-1,2,3,4-tetraaminobutane, 10 , by catalytic hydrogenation in ethanol using 10% Pd/C as the catalyst. Since the reduction

SCHEME 4. Synthesis of *Threo*-1,2,3,4-tetraaminobutane (10).

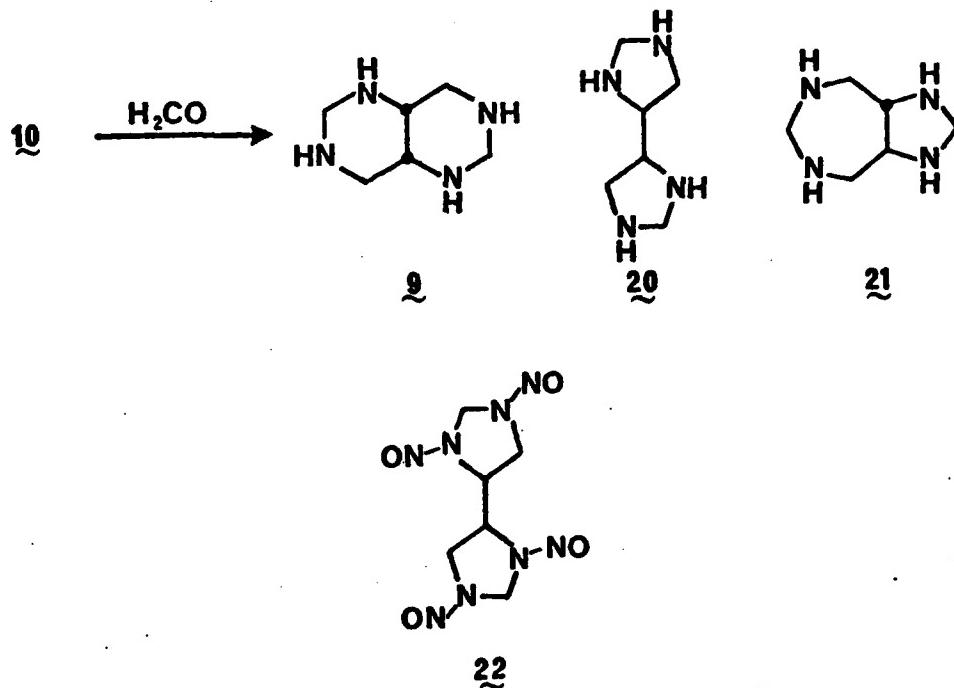


of a mole of azide requires one mole of hydrogen and releases one mole of nitrogen, no pressure drop is noted during the reduction. In order to introduce fresh hydrogen into the bottle, it is necessary to occasionally vent the bottle and refill it. The tetramine was characterized as its tetraacetamide derivative, 10b . Since the tetraamine was a hygroscopic liquid, it was difficult to get exact yield data. The best value for the combined yield of the displacement step and reduction step was 80-90%. The crude tetramine was used for the following synthetic procedures.

The best conditions for the formation of 9 from 10 were to dissolve 10 in a small amount of water and add the formaldehyde solution dropwise over a few minutes. This solution was stirred for an hour at 50°C . The solution was cooled to 5°C , and the required amount of sodium nitrite was added. After this had dissolved, the proper amount of 2M HCl was added in one portion. The tetranitroso product precipitated and was collected, washed, and dried. The yield for the product, based on starting tetrabenzenesulfonate, was 60-62%. The product was an amorphous powder and gave indications that it was a mixture of compounds. This is not unreasonable since there are three different ways for the *threo*-1,2,3,4-tetraaminobutane to cyclize, as summarized in Scheme 5. As shown from the results of the nitrolysis, the product is a mixture of the tetranitroso compounds, 8 and 22 .

The nitrolysis of the product proceeded in rather poor yield to give a crude product which was clearly a mixture of two compounds by ^1H NMR spectroscopy. The major product was isolated in pure form by fractional recrystallization from acetone. This compound has been assigned the *cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1) structure based upon its ^1H NMR spectrum which showed an AB quartet for the isolated methylene groups ($\text{C}_{2,6}$) with a large chemical shift difference (~ 1.9 ppm). This criterion has been used previously to assign structure in the analogous tetroxadecalin.⁵

SCHEME 5. Possible Products From the Reactions of 10^{\sim}
With 2 Moles of Formaldehyde.

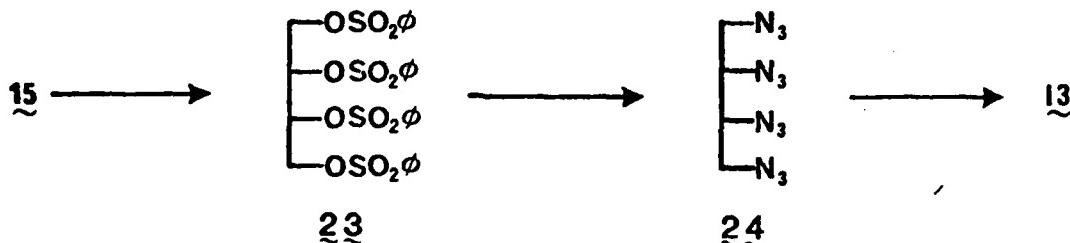


The minor product was isolated pure by preparative thin layer chromatography (TLC) of the mother liquors from the purification of 1^{\sim} . It was assigned the D-4,4'-bi-(1,3-dinitro-1,3-diazacyclopentane) structure, 3^{\sim} , on the basis of the small chemical shift difference for the protons of the isolated methylene groups (≈ 0.3 ppm).

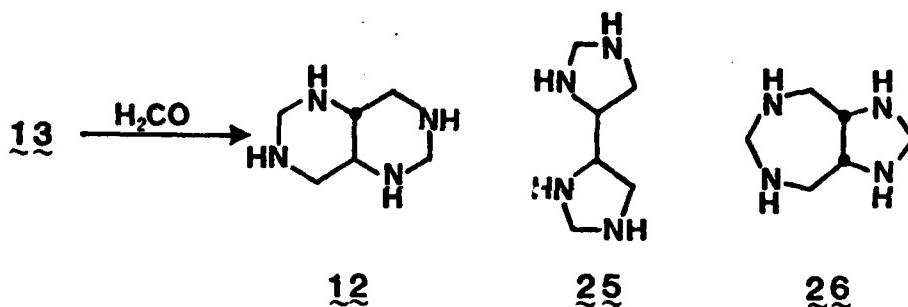
The ratio of 1^{\sim} to 3^{\sim} was observed to vary considerably depending on the conditions used for the reaction of the 10^{\sim} with formaldehyde. When this reaction was run for a short time cold ($0\text{--}10^{\circ}\text{C}$), the proportion of 3^{\sim} in the final product was increased quite substantially, even to the point where it was the major product. However, if the reaction was run as described above, the ratio of $\text{1}^{\sim}:\text{3}^{\sim}$ became approximately 10:1. This would seem to indicate that 20^{\sim} is the kinetically favored product of the reaction of 10^{\sim} with formaldehyde while 9^{\sim} is the thermodynamically favored product.

Trans-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (2)

In this case, the starting material, *meso*-erythritol, is commercially available at reasonable cost. The conversion of it to the desired *meso*-1,2,3,4-tetraaminobutane, 13^{\sim} , proceeded without complication through the tetrabenzenesulfonate, 23^{\sim} , and the tetraazide, 24^{\sim} , as outlined in Scheme 6. The details are given in the experimental section.

SCHEME 6. Synthesis of *Meso*-1,2,3,4-tetraaminobutane (13_{M}).

The reaction of the tetraamine, 13_{M} , with formaldehyde could again yield three products as summarized in Scheme 7. The reaction was run essentially as described for the *threo* isomer. This tetrinitroso product

SCHEME 7. Possible Products from the Reaction of 9_{M} with Formaldehyde.

was much better behaved. In fact, it could be recrystallized from DMF/H₂O and it gave a very nice IR spectrum. Nitrolysis of this product gave the crude *trans*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin, 2_{M} . The product could be recrystallized from DMF/H₂O to yield pure 2_{M} . Again, the assignment of structure was based upon the large (1.5 ppm) chemical shift difference for the protons of the isolated methylene groups (C_{2,6}). From the mother liquors of the recrystallization of 2_{M} , another product was isolated by preparative TLC. Small amounts of this product could also be obtained by further diluting the quench liquid and chilling overnight. This product was assigned the *meso*-4,4'-bi-(1,3-dinitro-1,3-diazacyclopentane) structure, 4_{M} , on the basis of the small shift difference (0.3 ppm) between the protons of the isolated methylene groups. The ratio of 2_{M} to 4_{M} can be estimated to be 20:1 from the ¹H NMR of the crude 2_{M} .

Physical and Chemical Properties of 1, 2, 3, and 4

The physical and chemical properties of compounds 1_{M} , 2_{M} , 3_{M} , and 4_{M} that have been determined are summarized in Table 1.

TABLE 1. Physical and Chemical Properties
of 1, 2, 3, and 4.

	mp (°C)	Heat of formation Kcal/mole	Impact sensitivity (2.5 kg wt)	Density (g/cc)
1	236-237	+19.4	16.4	1.78
2	251-252	+26.5	65.0	1.75
3	213-214	+33.0	...	1.64
4	198-199

DISCUSSION

SYNTHESIS

The successful synthesis of 1 and 2 clearly demonstrates that the methodology which we had developed previously for the synthesis of 1,3-dinitro-1,3-diazacycloalkanes is applicable to more complex systems. We now plan to extend this methodology to even more complicated systems.

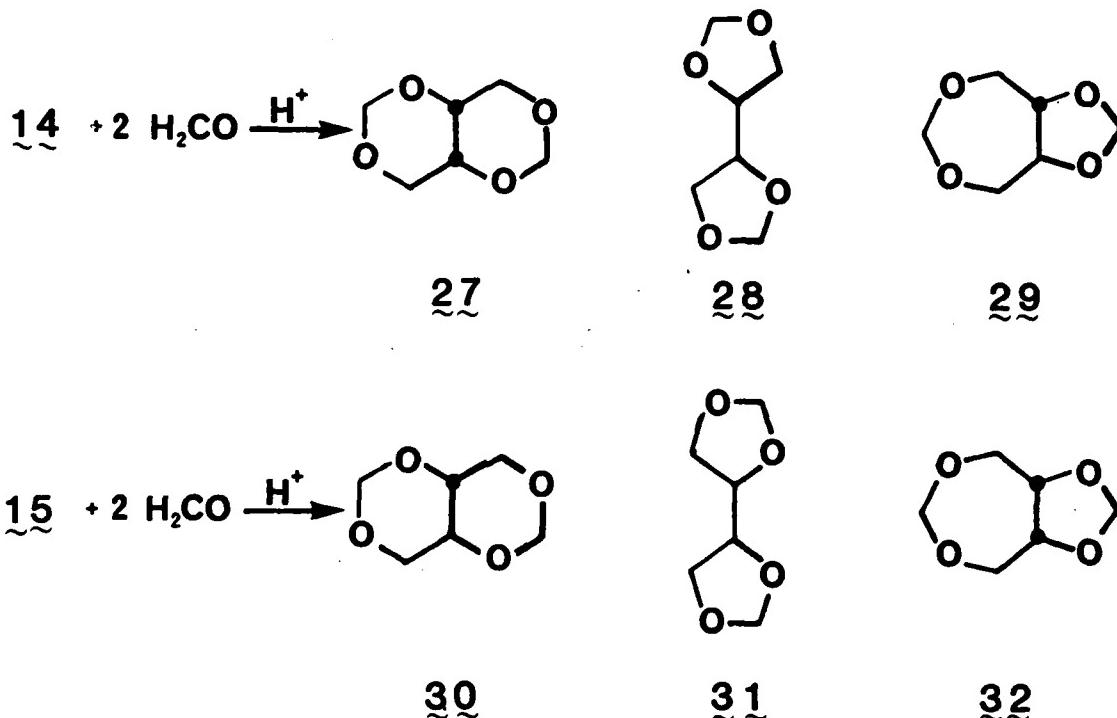
An interesting comparison can be made between this work and similar work on the reaction of threitol and erythritol with formaldehyde.⁵⁻⁷ As in this work there are three possible products from each reaction as summarized in Scheme 8. In the case of threitol, it has been found that the sole isolated product is the *cis*-1,3,5,7-tetraoxodecalin, 2.⁷ We observed that the reaction of *threo*-1,2,3,4-tetraaminobutane, 10, with formaldehyde gives a mixture of the tetraazadecalin, 9, and bi-(1,3-diazacyclopentane), 20, and that the ratio of 9:20 depends upon the

^{6a} I. J. Burden and J. Fraser Stoddart. "Isomerism in Bicyclic Diacetals, Part 1. 1,3:2,4- and 1,4:2,3-Di-O-Methylene Erythritol," *J. Chem. Soc., Perkins 1* (1975), pp. 666-674.

^{6b} I. J. Burden and J. Fraser Stoddart. "Constitutional Isomerism in Bicyclic Diacetals and the Conformational Behavior of Cis-Fused 1,3,6,8-Tetraoxabicyclo[5.3.0]decanes," *Chem. Comm.*, 1974, pp. 863-864.

⁷ R. B. Jensen, et al. "Reactions Between Formaldehyde and Polyhydric Alcohols, I. Five-, Six-, Seven-, and Twelve-Membered Cyclic Acetals from Meso-Erythritol and Formaldehyde," *Acta Chemica Scandinavica B* 29, 1975, pp. 373-378.

SCHEME 8. Possible Products From the Reaction of Threitol and Erythritol with Formaldehyde.



reaction conditions. Since the reaction of threitol with formaldehyde was run under conditions which should favor the formation of the thermodynamic product (reflux, acid catalysis) these results compare favorably with ours run at higher temperatures where we obtained a 10:1 mixture of 9 and 20. The reaction of erythritol with formaldehyde has been found to give an \approx 10:1 mixture of the *trans*-1,3,5,7-tetraoxodecalin, 30, and the 1,3-dioxalano-1,3-dioxepane, 32,^{6,7} whereas we obtained a 20:1 mixture of the tetraazadecalin, 12, and the bi-(1,3-diazacyclopentane), 25, and none of the 5:7 fused compound 26. The reasons for these differences in the erytho cases are not clear.

PHYSICAL AND CHEMICAL PROPERTIES

Melting Points

As might be expected, all four compounds have relatively high melting points with both decalins (1 and 2) having higher melting points than the bi-cyclopentanes (3 and 4). Compound 2 has one of the highest melting points of the known polynitramines.

Densities

According to the Holden method,⁸ compounds 1-4 have the same predicted density of 1.74 g/cc. The measured densities vary considerably from this value (see Table 1). That 1 has a density greater than 2 is in line with the fact that *cis*-decalin, 33, has a higher density than *trans*-decalin, 34.⁹



That 3 should have such a low density is in accord with the observation that compounds of this type tend to have lower densities than the parent compounds because the rings are forced to be perpendicular to each other. The densities of some other bi-compounds and the parent compounds follow.¹⁰⁻¹² We have measured and included the density of 1,3-dinitro-1,3-diazacyclopentane, 38, the parent compound of 3.

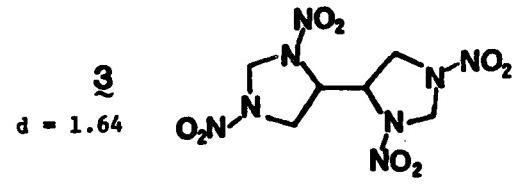
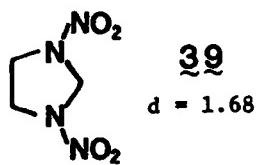
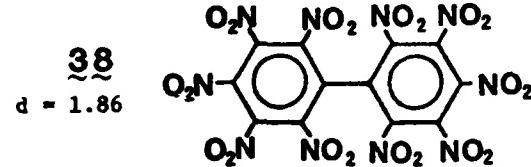
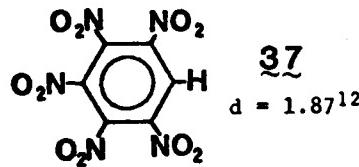
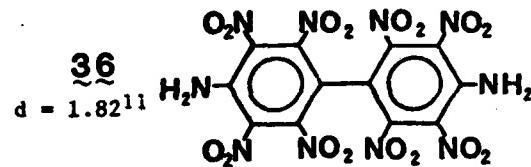
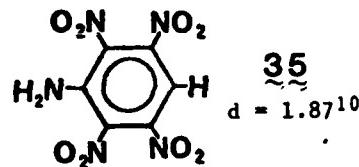
⁸ Naval Surface Weapons Center. *Estimation of Normal Densities of Explosive Compounds from Empirical Atomic Volumes*, by D. A. Cichra, J. R. Holden and C. Dickinson. Silver Spring, Md., NSWC, 1980. 39 pp. (NSWC Report TR79-273, publication UNCLASSIFIED.)

⁹ The Chemical Rubber Co. *Handbook of Chemistry and Physics*, 45th ed. Robert C. Weast, ed. Cleveland, Ohio, 1964, p. C281.

¹⁰ Lawrence Livermore National Laboratory. *LLNL Explosive Handbook. Properties of Chemical Explosives and Explosive Simulants*, by B. M. Dobratz. Livermore, Calif., LLNL, March 1981. (Report No. UCRL-52997, publication UNCLASSIFIED.)

¹¹ Naval Weapons Center. *Synthesis and Properties of a New High Explosive, 4,4'-Diamino-2,2',3,3',5,5',6,6'-octanitrobiphenyl (CL-12)*, A. T. Nielsen, et al. China Lake, Calif., NWC, April 1981. 22 pp. (NWC TP 6212, publication UNCLASSIFIED.)

¹² C. Coon, SRI International, (unpublished observations).

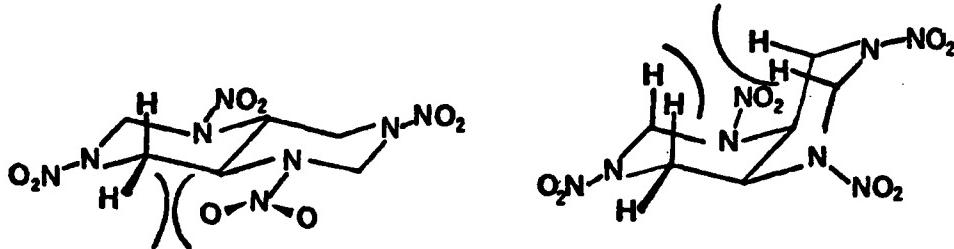


Impact Sensitivities

Impact sensitivities were measured only on compounds 1 and 2. The great difference (16 vs. 65 cm) in the values for 1 and 2 would seem to be unreasonable. However, it should be noted that there was a great difference in the crystal sizes of samples used for this measurement. The sample of compound 1 we used was composed of large crystals ($\approx 1 \text{ mm}^2$) while the sample of 2 was a microcrystalline material. Since several studies have noted a relationship between crystal size and impact sensitivity,¹¹ the large difference between the measured values for 1 and 2 may in part be simply a function of particle size and not a true measure of their respective inherent impact sensitivities.

Heats of Formation

The measured heats of formation of 1, 2, and 3 seem to reflect the amount of steric strain present in the molecules as estimated by inspection of molecular models of the compounds. The *trans*-decalin, 2, is highly strained because of a very unfavorable interaction between the 1,5 nitro groups and the 4,8 methylene groups. As shown below, this interaction is absent in the *cis*-decalin.



EXPERIMENTAL

Densities were determined on a Systems, Science, and Software type 6102 gas pycnometer and are the average of three separate determinations. ^1H NMR spectra were recorded on a Varian EM-360 or on an XL-100 NMR spectrometer. Impact sensitivities were measured on 35-mg samples on a Model 12 impact machine. Heats of combustions were determined on a Parr adiabatic bomb calorimeter. IR spectra were recorded on a PE 137 spectrometer. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tennessee.

DIETHYL-2,3-O-CYCLOHEXYLIDINE-L-TARTRATE (16)

A solution of diethyl tartrate (206.19 g, 1 mole) and cyclohexanone (147.2 g, 1.5 mole) dissolved in 600 ml of benzene was prepared. To this solution 5 g of p-toluene sulfonic acid monohydrate was added. The solution was refluxed and the water collected by means of a Dean-Stark trap. After the water had stopped collecting (16 hours) the solution was cooled, washed with 10% NaOH (100 ml), then dried over MgSO_4 . The solution was filtered and the solvent removed at reduced pressure. The crude product was vacuum distilled to give 175.6 g of product (0.61 mole, 61%) with a b.p. of 124-126°C at 0.15 mm (lit^5 142°C at 10 mm).

IR (See Appendix A, Figure A-1).

NMR (See Appendix B, Figure B-1).

L-THREITOL (14)

Diethyl-2,3-O-cyclohexylidine tartrate (57.2 g, 0.2 mole) was dissolved in 100 ml of dry tetrahydrofuran (THF). This solution was added dropwise over a 1-hour period to a well-stirred slurry of 14.0 g of

lithium tetrahydroaluminate and 400 ml of dry THF. The reaction mixture was stirred for 2 additional hours then the reaction was worked up by the careful addition of water (14 ml), 15% NaOH (14 ml), and more water (28 ml). The resulting slurry was filtered and the solid material reslurried with 200 ml hot THF and refiltered. The combined THF solutions were concentrated at reduced pressure to yield the crude 2,3-O-cyclohexylidine-L-threitol, 17. The IR and NMR spectra of the crude product indicated it was very pure (see Appendix A, Figure A-2 and Appendix B, Figure B-2). Water (200 ml) and 1 ml of concentrated hydrochloric acid was added to the crude 17. This mixture was heated and the cyclohexanone/water azeotrope distilled off over a 1-hour period. The solution was cooled and extracted with 100 ml diethyl ether. The aqueous phase was concentrated at reduced pressure to yield a thick oil which crystallized upon the addition of 200 proof alcohol. The alcohol was removed at reduced pressure to yield the crude L-threitol, 20.42 g (0.18 mole, 90%). A small sample was recrystallized from 95% EtOH to give needles with a m.p. of 86-87°C (lit⁵ 86-88°C).

IR (See Appendix A, Figure A-3).

NMR (See Appendix B, Figure B-3).

L-THREITOL-TETRABENZENESULFONATE (18)

L-threitol (12.2 g, 0.1 mole) was dissolved in 200 ml dry pyridine. This solution was cooled (salt-ice bath) and benzenesulfonyl chloride (75 ml, 0.6 mole) was added dropwise over a 1-hour period. The cooling bath was removed and the mixture was stirred at room temperature for 16 hours. The solution was poured onto a mixture of 300 g ice and 100 ml concentrated HCl. The product oiled out. The aqueous layer was decanted from the oil. The oil was dissolved in a hot mixture of methanol (300 ml) and acetone (50 ml). The volume of the solution was reduced to 200 ml and the product allowed to crystallize. The product was collected and dried. The yield was 48.24 g (0.07 mole, 70%) of material with a m.p. of 112-114°C.

Analysis calculated for C₂₈H₂₆O₁₂S₄: C, 49.26; H, 3.81.
Found: C, 49.18; H, 4.00.

IR (See Appendix A, Figure A-4).

NMR (See Appendix B, Figure B-4).

THREE - 1,2,3,4-TETRAAZIDOBUTANE (19)

L-threitol tetrabenzenesulfonate (20.46 g, 0.03 mole), sodium azide (10 g, 0.15 mole) and dry DMF (200 ml) were placed in a 500 ml flask. This solution was stirred at 100°C for 4 hours then cooled to 10°C and

diluted with 250 ml H₂O. The H₂O/DMF solution was extracted with ether (4 x 100 ml) and the combined ether extracts bath extracted with water (2 x 50 ml). The ether solution was dried over MgSO₄, filtered, and the ether removed at reduced pressure to give the crude *threo*-1,2,3,4-tetraazidobutane. The products contain a fair amount of DMF so no yield data can be obtained. No attempt was made to purify the product because of the known hazards of polyazido compounds.

IR (See Appendix A, Figure A-5).

NMR (See Appendix B, Figure B-5).

THREO-1,2,3,4-TETRAAMINOBUTANE (10)

The crude tetraazide was dissolved in 120 ml, 95% ethanol in a 500 ml Parr bottle and 1 g of 10% Pd/C was added. This mixture was hydrogenated at 55 psi with the tank shut off. Every hour the bottle was vented and fresh hydrogen was introduced. After 4 hours, the solution was filtered and the solvent removed at reduced pressure to yield the crude *threo*-1,2,3,4-tetraaminobutane. A small portion of this reacted with acetic anhydride gave the tetraacetamide derivative with a m.p. of 242-244°C.

Analysis calculated for C₁₂H₂₂N₄O₄: C, 50.33; H, 7.74; N, 19.57.
Found: C, 49.94; H, 7.92; N, 19.17.

IR (See Appendix A, Figure A-6).

NMR (See Appendix B, Figure B-6).

CIS-1,3,5,7-TETRANITROSO-1,3,5,7-TETRAAZADECALIN (8) and
D-(4,4')-BI-(1,3-DINITROSO-1,3-DIAZACYCLOPENTANE) (22)

The crude 10 was dissolved in 30 ml of distilled water and 5.0 g of 37% aqueous formaldehyde solution was added dropwise over a 5-minute period. The mixture was stirred at 50°C for an hour. The solution was cooled to 5°C and sodium nitrite (8.4 g, 0.12 mole) was added. When the sodium nitrite had completely dissolved, 60 ml of 2N HCl was added in one portion. The product precipitated and was collected and washed well with water. After drying the product weighs 4.61-4.80 g (0.018-0.019 mole, 60-62%).

IR (See Appendix A, Figure A-7).

NMR (See Appendix B, Figure B-7).

*CIS-1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZADECALIN (1) and
D-4,4'-(1,3-DINITRO-1,3-DIAZACYCLOPENTANE) (3)*

The crude product from the previous step was ground into a fine powder. A 3 g portion (0.012 mole) was then added over a 10-minute period to 45 ml of well stirred 100% nitric acid which was maintained at -30°C by means of a dichloroethane dry ice slush. After the addition was complete, the dichloroethane bath was removed and replaced with an ice water bath. The solution was stirred at 0°C for 20 minutes then the ice water bath was removed and replaced with a 40°C hot water bath. The mixture was stirred at 40°C for 15 minutes then poured onto 200 g of ice. After the ice had melted the quench solution was diluted to 500 ml. The crude product was collected by vacuum filtration. A second crop could be collected by allowing the mother liquor to stand over night. The first crop of crude product weighed 2.26-2.46 g after drying. The second crop weighed 0.75 g after drying. The total yield of crude product is approximately 3.02 g (0.009 mole, 80%). Depending upon the conditions used for the reaction of 1 with formaldehyde, the ratio of 1:3 varies from 15:1 to ≈1:1.

NMR (See Appendix B, Figures B-8 and B-9).

Separation of 1 and 3

Mixtures Rich in 1. The entire crude product (\approx 3.0 g) was dissolved in acetone and filtered to remove insoluble materials. The solution was concentrated to 15 ml and a seed crystal of pure 1 was added. The solution was allowed to slowly evaporate until the volume of liquid was \approx 5 ml. The liquid was removed by means of a pipette and the crystals were washed twice with 10 ml of ethyl acetate. The crystals were dried in vacuum to give 1.80 g of pure 1 with a m.p. of 234-235°C.

Analysis calculated for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.12; N, 34.78.
Found: C, 22.60; H, 3.20; N, 34.83.

IR (See Appendix A, Figure A-8).

NMR (See Appendix B, Figure B-10).

Mixtures Rich in 3. The crude product was dissolved in 20 ml acetone and filtered to remove insoluble materials. The solution was warmed to reflux and water was added dropwise until the solution remained turbid. More acetone was added and the solution was allowed to cool. The product was collected and washed with acetone. The pure 3 melts at 213-214°C.

Analysis calculated for $C_6H_{10}N_8O_8$: C, 22.36; H, 3.13; N, 34.78.
Found: C, 22.67; H, 3.12; N, 35.01.

IR (See Appendix A, Figure A-9).

NMR (See Appendix B, Figure B-11).

Mixture of 1 and 3. In addition, small amounts of mixtures of 1 and 3 can be separated by preparative TLC using 2 mm silica gel plate and a 50:30 THF-hexane solvent system. The RFs of 1 and 3 are approximately 0.2 and 0.7, respectively.

MESO-ERYTHRITOL TETRABENZENESULFONATE (23)

Meso-erythritol (12.2 g, 0.1 mole) was added to 200 ml of dry pyridine. This slurry was maintained below 5°C by an ice bath while 75 ml of benzenesulfonyl chloride was added dropwise over a 30-minute period. The cooling bath was removed and the mixture stirred at room temperature for 4 hours. The mixture was then poured onto a mixture of 200 g of ice and 100 ml of concentrated HCl. The product precipitated as an oily solid. This crude product was collected by vacuum filtration and then slurried with 300 ml of methanol. The product was recollected and dried. It weighed 60.2 g (0.088 mole, 88%) and melted at 184-185.5°C.

Analysis calculated for C₂₈H₂₆O₂₄S₄: C, 49.27; H, 3.81.
Found: C, 49.46; H, 3.91.

IR (See Appendix A, Figure A-10).

NMR (See Appendix B, Figure B-12).

ERYTHRO-1,2,3,4-TETRAAZIDOBUTANE (24)

Erythritol tetrabenzenesulfonate (20.4 g, 0.03 mole) and sodium azide were placed in a 500 ml round-bottom flask, dry DMF (200 ml) was added, and the contents were stirred at 110°C for 4 hours. The mixture was cooled and diluted with 300 ml of cold water. The solution was extracted with four 100-ml portions of ether. The ether extracts were combined and both extracted with two 50-ml portions of water. The ether layer was dried over MgSO₄, filtered, and the solvent removed at reduced pressure to give the crude *erythro*-1,2,3,4-tetraazidobutane. No attempt was made to purify the compound because of the known sensitivity of polyazido compounds.

IR (See Appendix A, Figure A-11).

NMR (See Appendix B, Figure B-13).

MESO-1,2,3,4-TETRAAMINOBUTANE (13)

The crude tetraazidobutane was dissolved in 100 ml of 95% ethanol and 1 g of 10% Pd/C was added. This solution was hydrogenated at 55 psi in a Parr apparatus with the tank shut off from the bottle. Every hour the bottle was vented and fresh hydrogen introduced. After 4 hours, the solution was filtered and the solvent removed at reduced pressure to give the crude *erythro*-1,2,3,4-tetraaminobutane. A small portion was reacted with acetic anhydride to give the tetraacetamide with a m.p. of 310-311°C.

Analysis calculated for $C_{12}H_{22}N_4O_4$: C, 50.33; H, 7.75; N, 19.57.
Found: C, 50.29; H, 7.65; N, 19.51.

IR (See Appendix A, Figure A-12).

NMR (See Appendix B, Figure B-14).

TRANS-1,3,5,7-TETRANITROSO-1,3,5,7-TETRAAZADECALIN (11)

The crude *erythro*-1,2,3,4-tetraaminobutane was dissolved in 30 ml of water and this solution was cooled to 5°C. Thirty-seven percent aqueous formaldehyde (4.06 g, 0.06 mole) was then added dropwise with stirring. The cooling bath was removed and the mixture stirred at 50°C for 1 hour. Sodium nitrite (8.28 g, 0.12 mole) was added to the solution. When the sodium nitrite had completely dissolved the solution was cooled to 5°C and a solution of 11.5 g concentrated hydrochloric acid (diluted) 50 ml was added. A precipitate formed almost immediately. After 10 minutes of stirring, the product was collected by vacuum filtration and washed well with water. After drying, the product weighed 2.62 g (0.010 mole, 33%). The material could be recrystallized from DMF/H₂O to give light yellow platelets with a m.p. of 200-202°C (dec).

IR (See Appendix A, Figure A-13).

NMR (See Appendix B, Figure B-15).

TRANS-1,3,5,7-TETRANITRO-1,3,5,7-TETRAAZADECALIN (2)

Fifteen ml of 100% nitric acid was placed in a 50 ml Erlenmeyer flask. A magnetic stirring bar was added and the contents cooled to -30°C by means of a dichloroethane/dry ice slush. *Trans*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin was added to this solution over 10 minutes. The dichloroethane/dry ice bath was replaced with an ice water bath. After stirring at 0°C for 30 minutes, the mixture was stirred at 50°C for 10 minutes. The solution was then poured onto 30 g of ice. After the ice had melted the product was collected by vacuum filtration

NWC TP 6416

and was washed well with water. After drying, the crude product weighed 0.66 g. The product was purified by dissolving in warm DMF (60°C) and by adding water until turbid. After cooling to 0°C, the crystals were collected. The purified product weighed 0.41-0.45 g and melted at 252-254°C.

Analysis calculated for C₆H₁₀N₈O₈: C, 22.36; H, 3.13; N, 34.78.
Found: C, 22.62; H, 3.21; N, 34.62.

IR (See Appendix A, Figure A-14).

NMR (See Appendix B, Figure B-16).

MESO-4,4'-(1,3-DINITRO-1,3-DIAZACYCLOPENTANE) (4)

By diluting the mother liquors from the recrystallization of γ with water, an impure material could be isolated. This material could be purified by preparative TLC (silica gel G₁/THF-hexane) to give pure γ with a m.p. of 198-199°C.

Analysis calculated for C₆H₁₀N₈O₈: C, 27.36; H, 3.13; N, 34.78.
Found: C, 27.52; H, 3.22; N, 34.82.

IR (See Appendix A, Figure A-15).

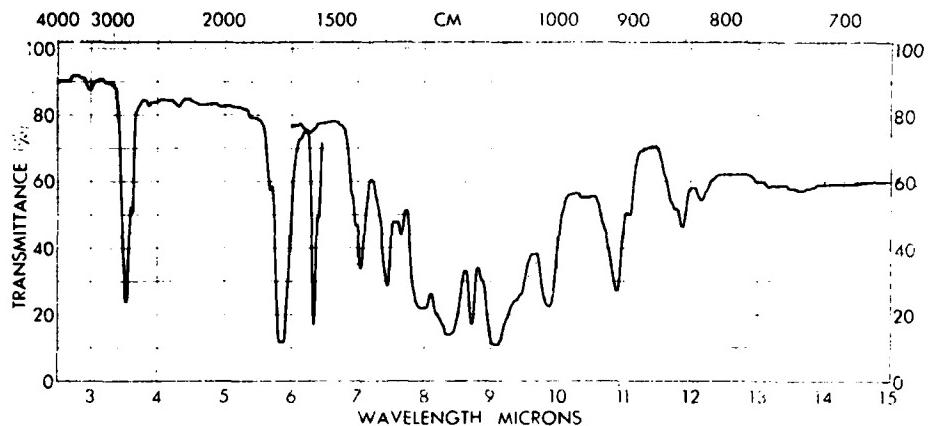
NMR (See Appendix B, Figure B-17).

NWC TP 6416

Appendix A

INFRARED SPECTRA OF COMPOUNDS

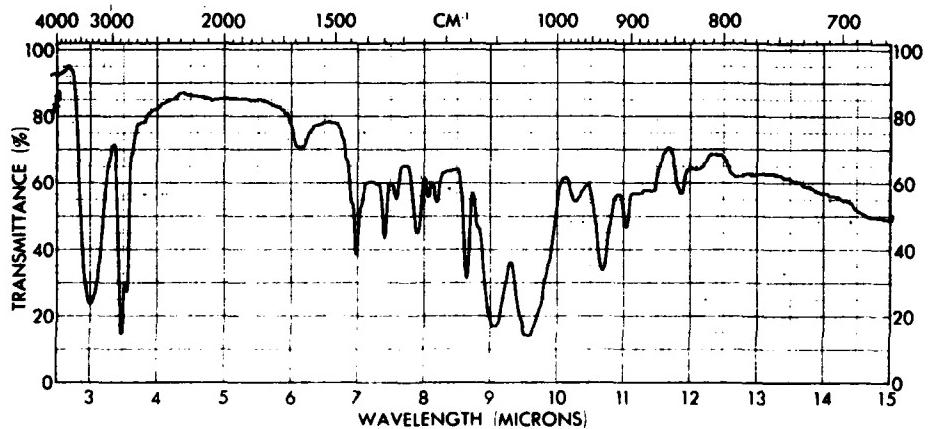
NWC TP 6416



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO.
SAMPLE		1.		SAMPLE
	PURITY	2.		
	PHASE	NEAT	DATE 5/24/62	
	THICKNESS		OPERATOR WILMER	

THE PERKIN ELMER CORPORATION, NORWALK, CONN.

FIGURE A-1. IR Spectrum of Diethyl-2,3,0-cyclohexylidine-L-tartrate (16).

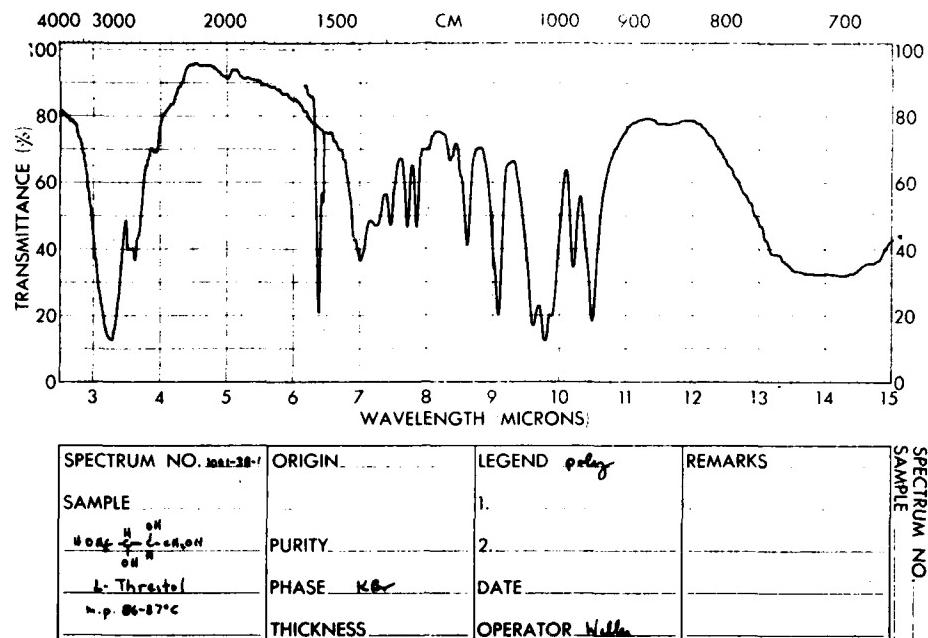


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO.
SAMPLE		1.		SAMPLE
	PURITY	2.		
	PHASE	NEAT	DATE	
	THICKNESS		OPERATOR	

THE PERKIN ELMER CORPORATION, NORWALK, CONN.

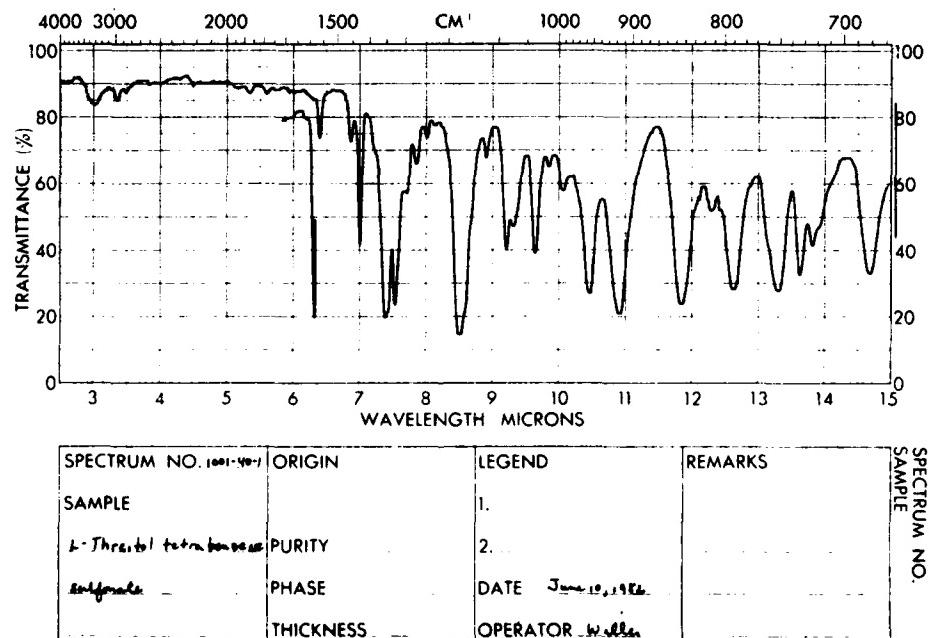
FIGURE A-2. IR Spectrum of 2,3-O-Cyclohexylidine-L-threitol (17).

NWC TP 6416



THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

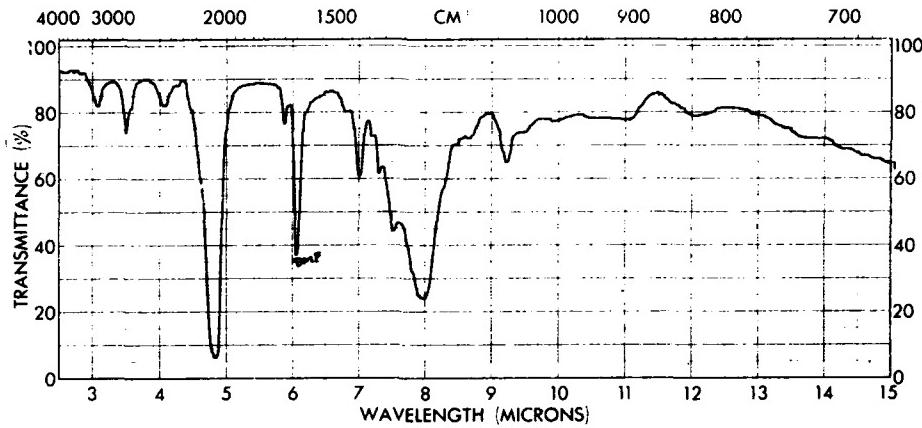
FIGURE A-3. IR Spectrum of L-Threitol (14).



THE PERKIN ELMER CORPORATION NORWALK, CONN.

FIGURE A-4. IR Spectrum of L-Threitol-tetrabenzenesulfonate (18).

NWC TP 6416

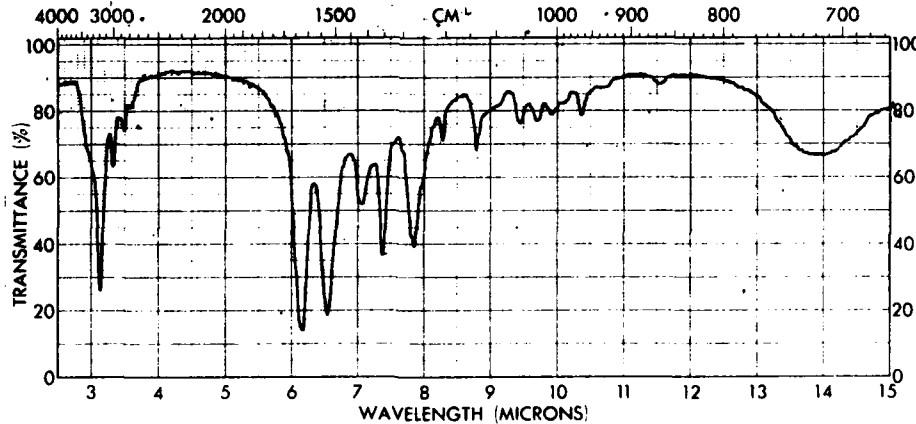


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SAMPLE
SAMPLE Ornate three		1.		
1,2,3,4-tetraazidobutane	PURITY	2.		
	PHASE film	DATE		
	THICKNESS	OPERATOR		

PART NO. 137-1281-A *

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

FIGURE A-5. IR Spectrum of Threo-1,2,3,4-tetraazidobutane (19).



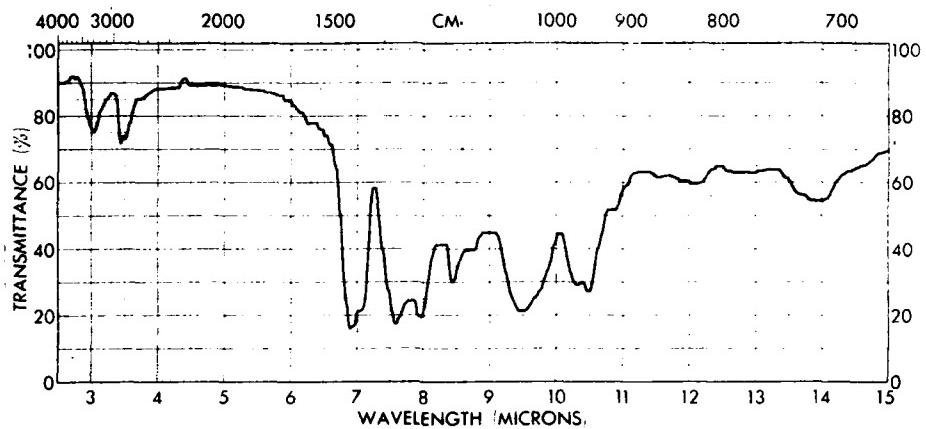
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SAMPLE
SAMPLE A "Threo"		1.		
CROCKED	PURITY	2.		
AC	PHASE KBr	DATE May 4, 82		
	THICKNESS	OPERATOR Weller		

PART NO. 137-1281-A *

THE PERKIN ELMER CORPORATION, NORWALK, CONN.

FIGURE A-6. IR Spectrum of Threo-1,2,3,4-tetraacetamidobutane (10b).

NWC TP 6416

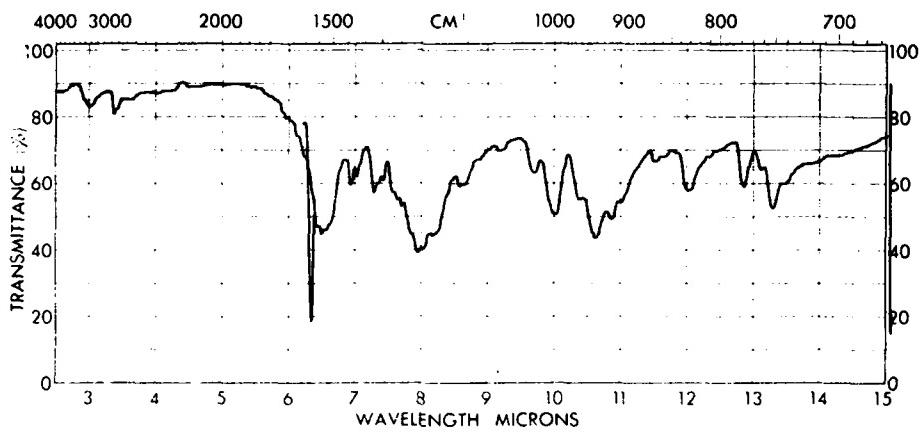


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO. SAMPLE
SAMPLE 	PURITY	1..		
	PHASE	2..		
	THICKNESS	DATE July 6 62		
		OPERATOR Waller		

PART NO. 137-1281 V-2

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

FIGURE A-7. IR Spectrum of a Mixture of *Cis*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (8) and *D*-(4,4')-bi-(1,3-dinitroso-1,3-diazacyclopentane) (22).



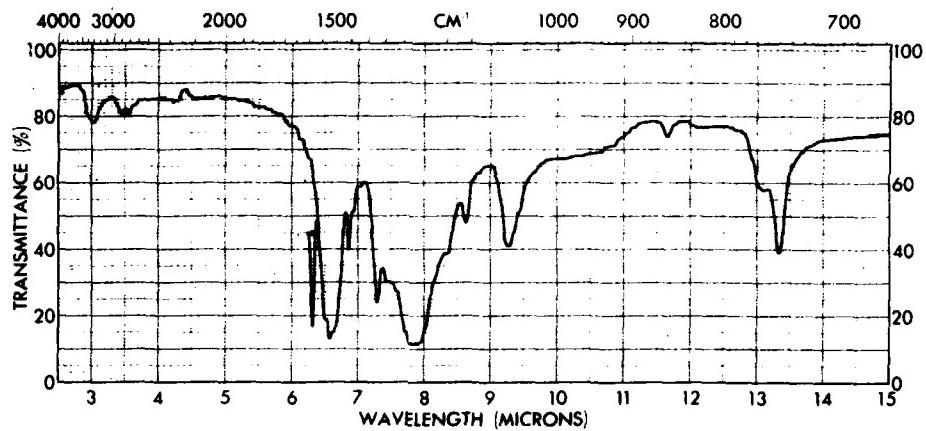
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO. SAMPLE
SAMPLE 	PURITY	1..		
	PHASE	2..		
	THICKNESS	DATE		
		OPERATOR		

PART NO. 137-1281 V-2

THE PERKIN ELMER CORPORATION, NORWALK, CONN.

FIGURE A-8. IR Spectrum of *Cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1).

NWC TP 6416

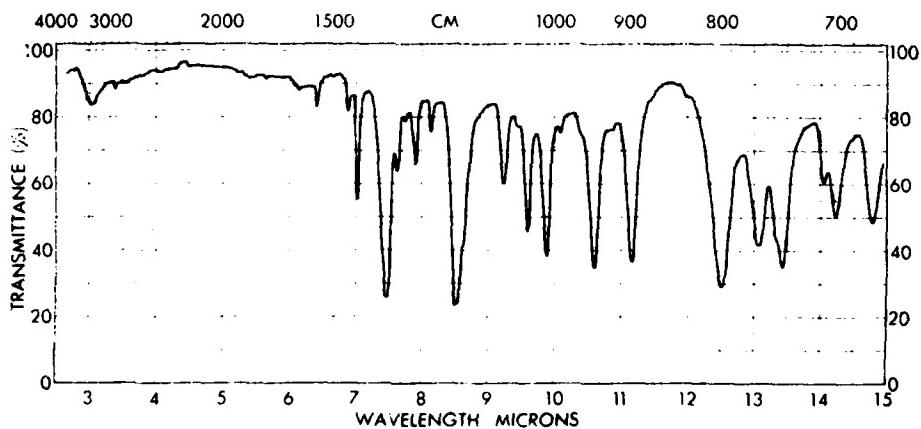


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO.
SAMPLE		1.		
PURITY		2.		
PHASE		DATE		
THICKNESS		OPERATOR		

PART NO. 137-1281 PL. 0

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

FIGURE A-9. IR Spectrum of D-4,4'-(1,3-dinitro-1,3-diazacyclopentane) (3).



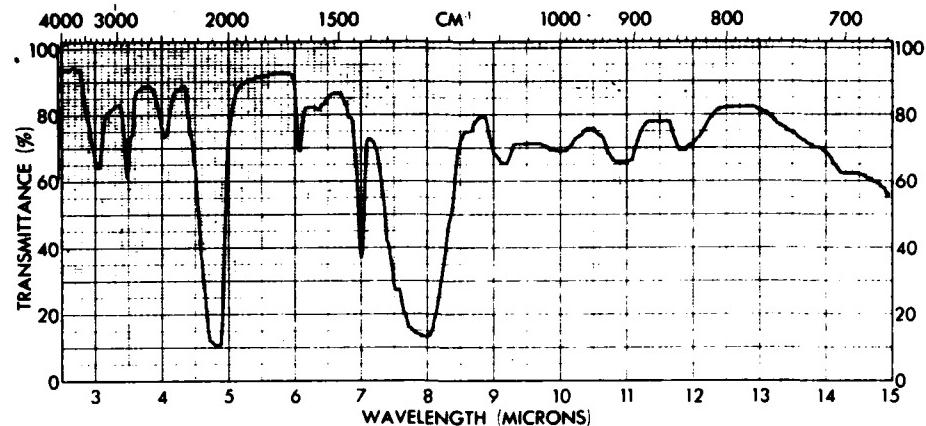
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO.
SAMPLE		1.		
PURITY		2.		
PHASE KBr		DATE 5-19-62		
THICKNESS		OPERATOR Miller		

PART NO. 137-1281

THE PERKIN ELMER CORPORATION, NORWALK, CONN.

FIGURE A-10. IR Spectrum of Meso-erythritol Tetrabenzenesulfonate (23).

NWC TP 6416

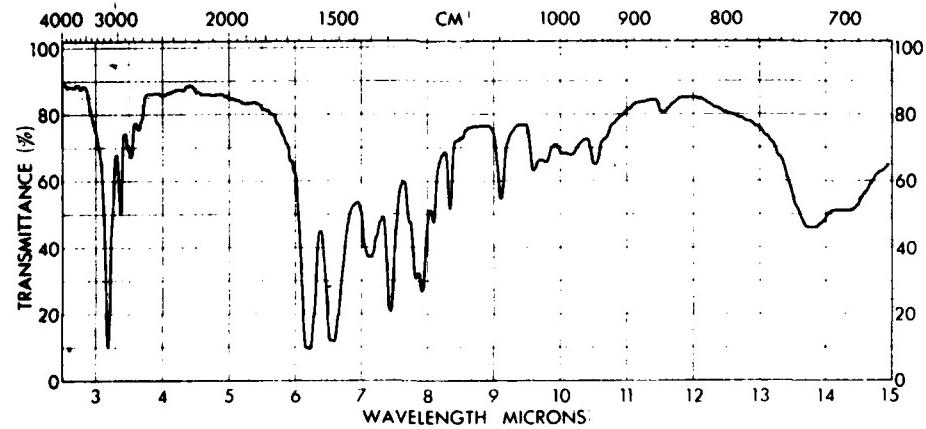


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO. SAMPLE
SAMPLE <i>Erythro</i> -		1.		
<i>1,2,3,4-tetraazido-butane</i>		2.		
PHASE <i>solid</i>		DATE <i>July 20, 82</i>		
THICKNESS		OPERATOR <i>Miller</i>		

PART NO 137-1281

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

FIGURE A-11. IR Spectrum of *Erythro*-1,2,3,4-tetraazadibutane (24).



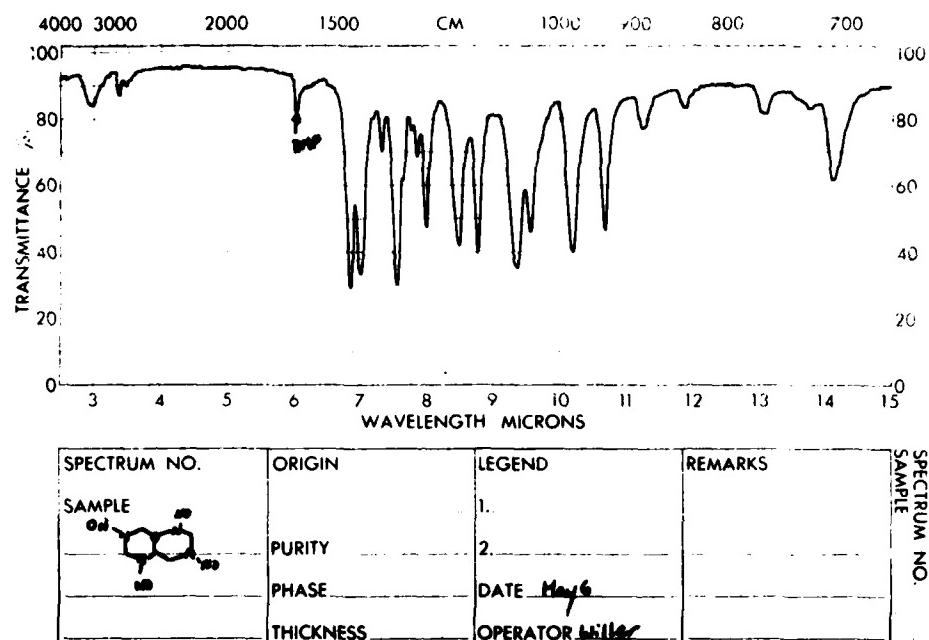
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS	SPECTRUM NO. SAMPLE
SAMPLE		1.		
<i>Meso</i> - <i>1,2,3,4-tetraacetamido-butane</i>		2.		
PHASE <i>solid</i>		DATE <i>July 20, 82</i>		
THICKNESS		OPERATOR <i>Miller</i>		

PART NO 137-1281

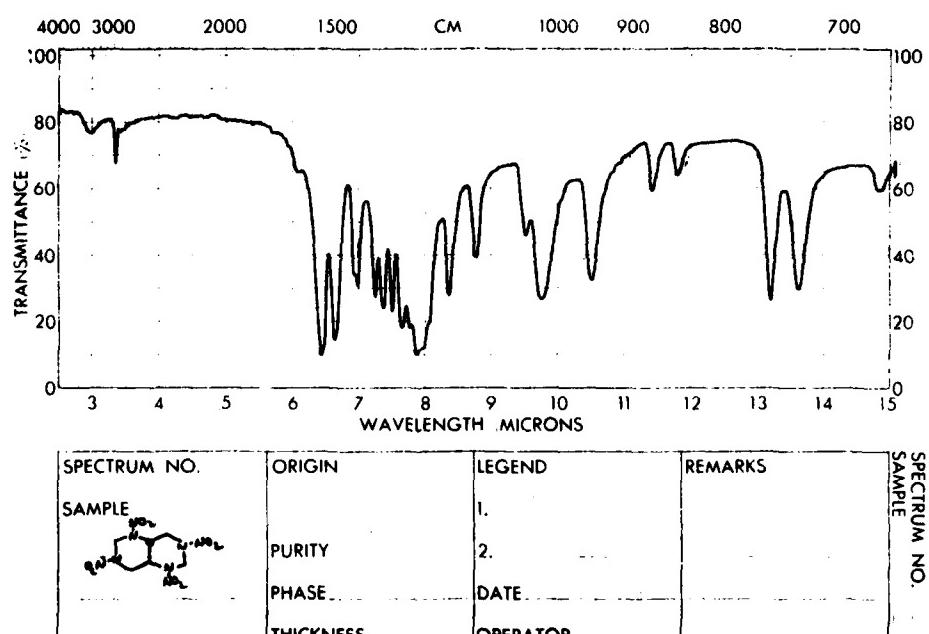
THE PERKIN ELMER CORPORATION, NORWALK, CONN.

FIGURE A-12. IR Spectrum of *Meso*-1,2,3,4-tetraacetamidobutane (13b).

NWC TP 6416



PART NO 137-1281 11- *
 THE PERKIN-ELMER CORPORATION, NORWALK, CONN.
FIGURE A-13. IR Spectrum of *Trans*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (1).



PART NO 137-1281
 THE PERKIN ELMER CORPORATION, NORWALK, CONN.
FIGURE A-14. IR Spectrum of *Trans*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (2).

NWC TP 6416

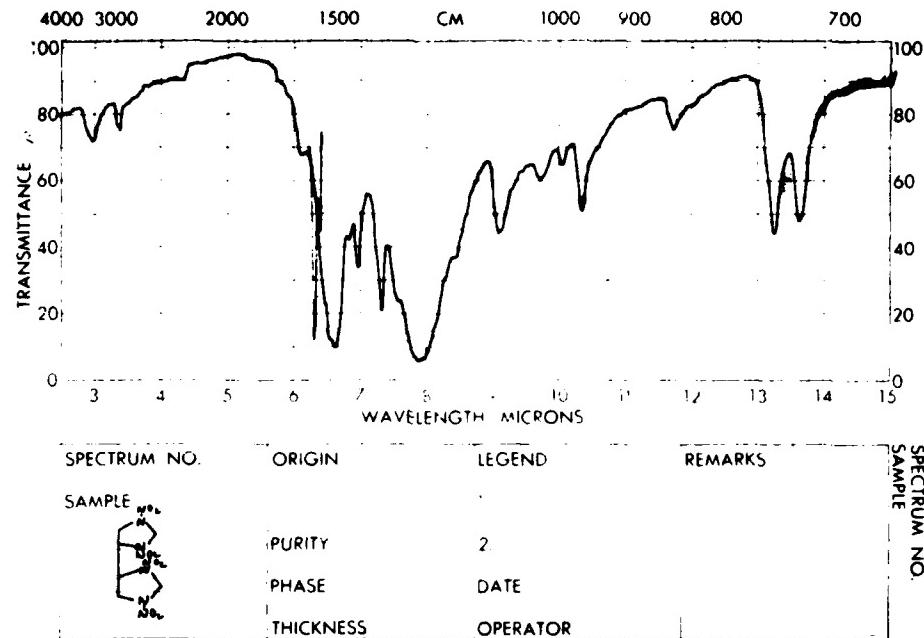


FIGURE A-15. IR Spectrum of *Meso*-4,4'-(1,3-dinitro-1,3-diazacyclopentane) (4).

NWC TP 6416

Appendix B

^1H NMR SPECTRA OF COMPOUNDS

NWC TP 6416

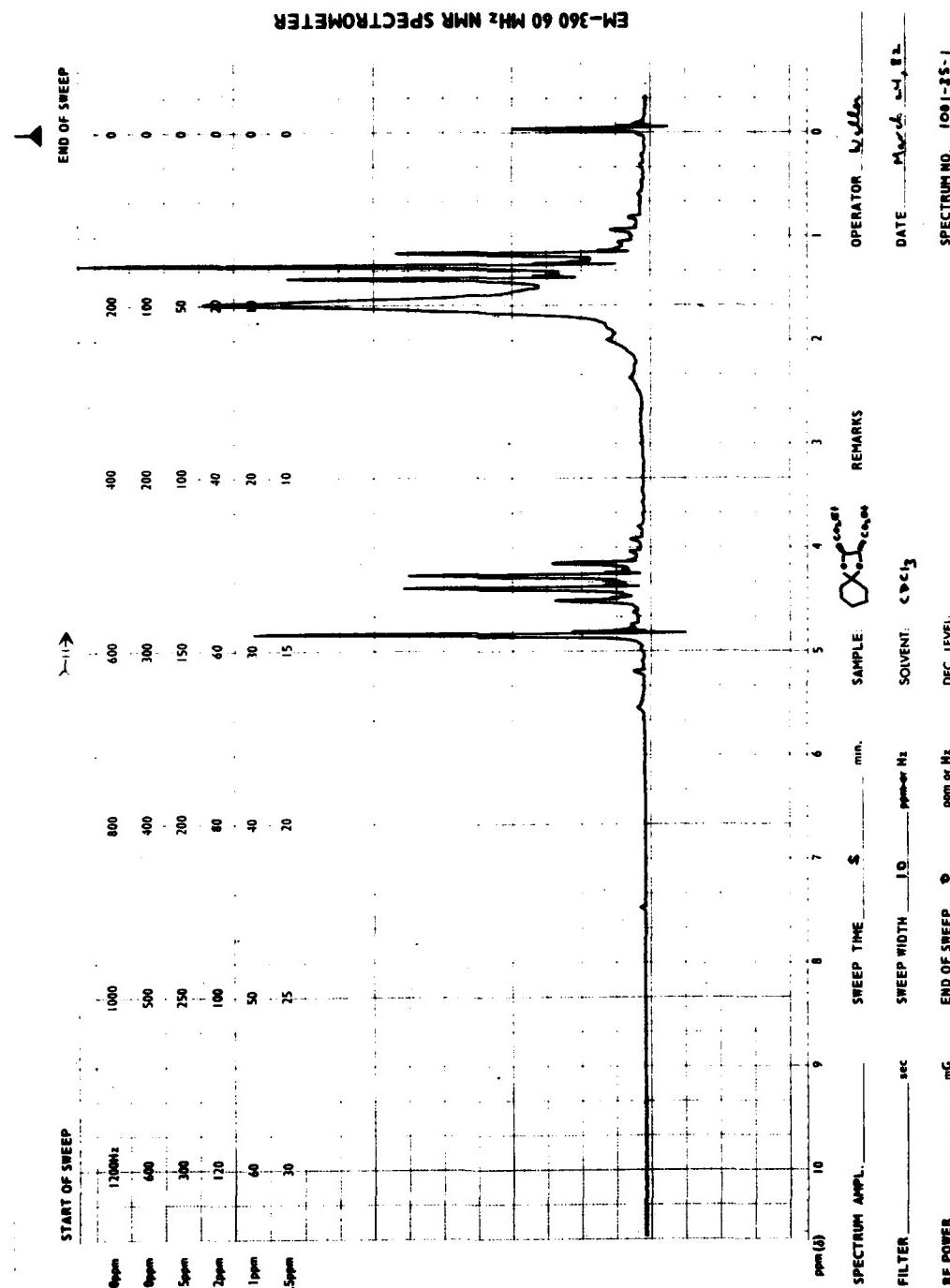


FIGURE B-1. NMR Spectrum of Diethyl-2,3-0-cyclohexylidine-L-tartrate (16).

NWC TP 6416

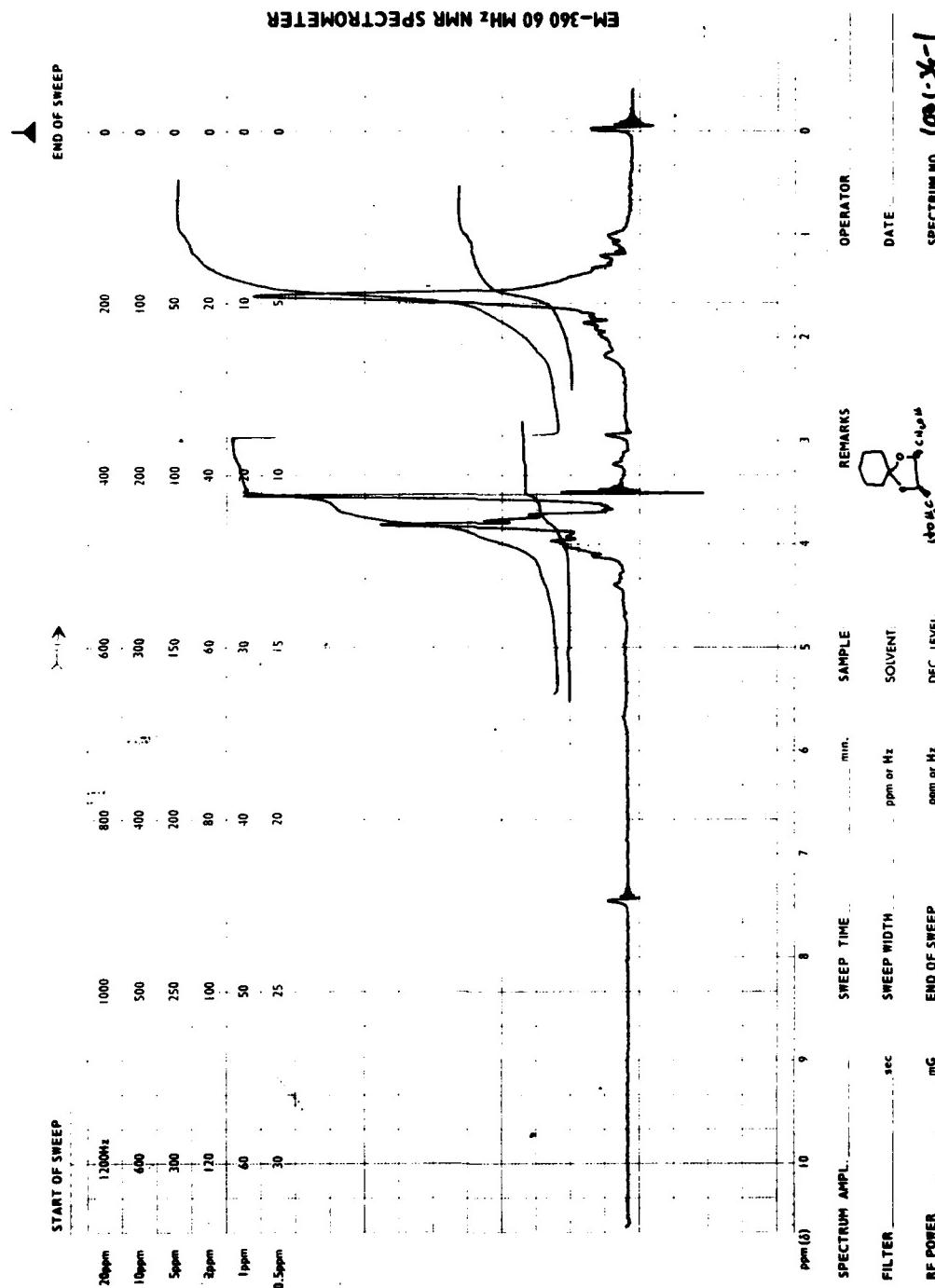


FIGURE B-2. NMR Spectrum of 2,3-O-Cyclohexylidene-L-threitol (1J).

NWC TP 6416

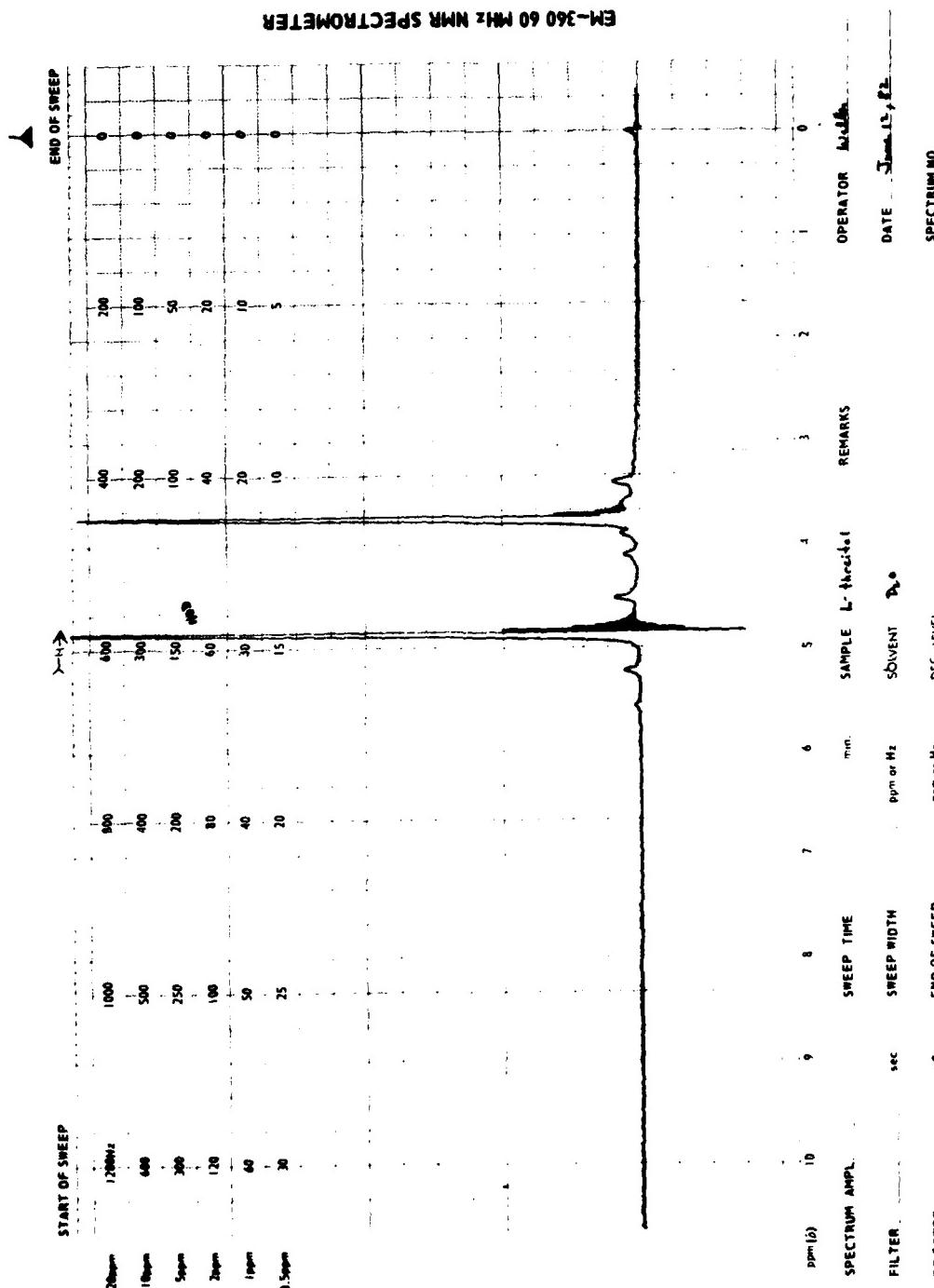


FIGURE B-3. NMR Spectrum of L-Threitol (14).

NWC TP 6416

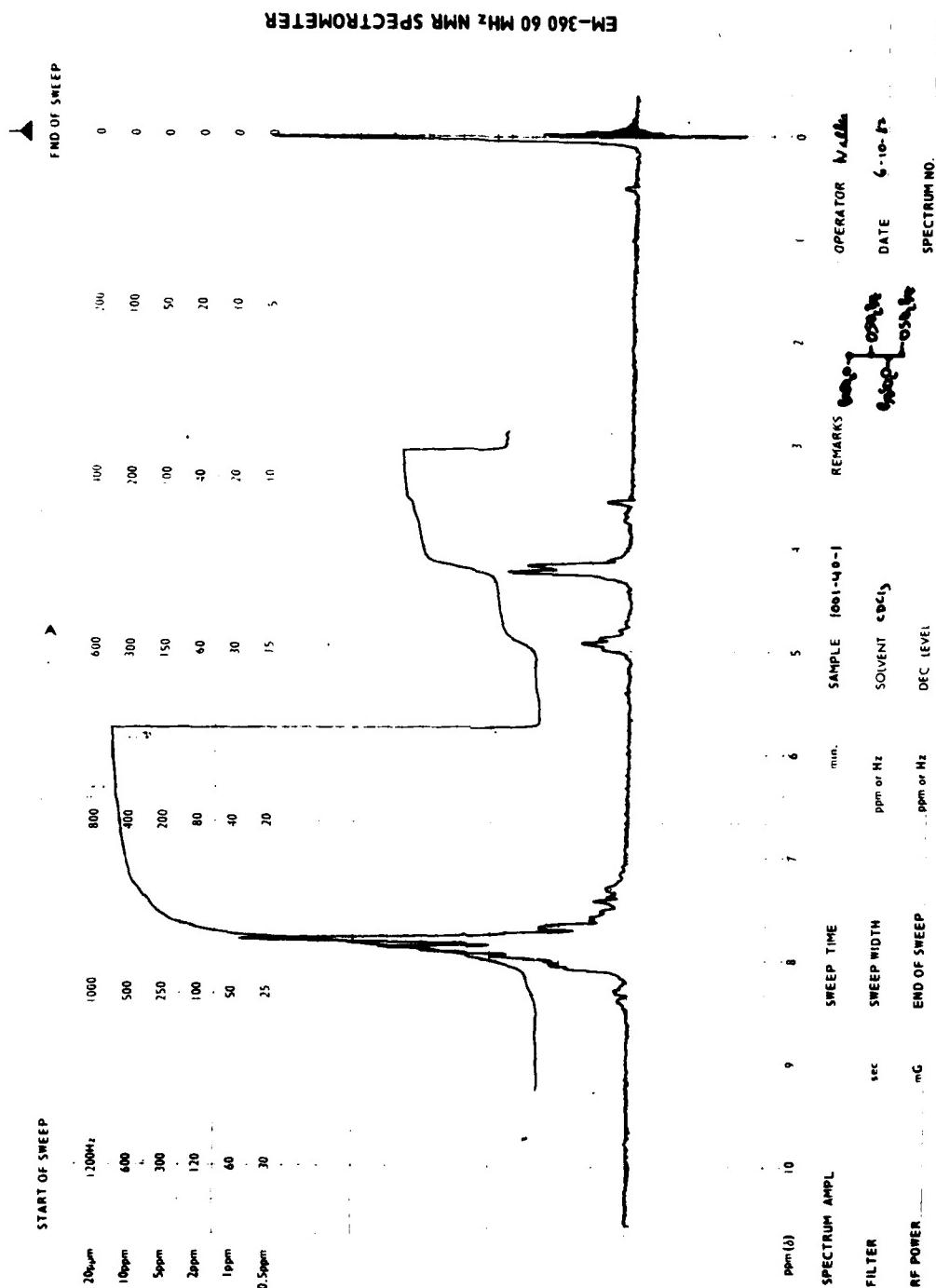


FIGURE B-4. NMR Spectrum of L-Threitol-tetrabenzenesulfonate (18).

NWC TP 6416

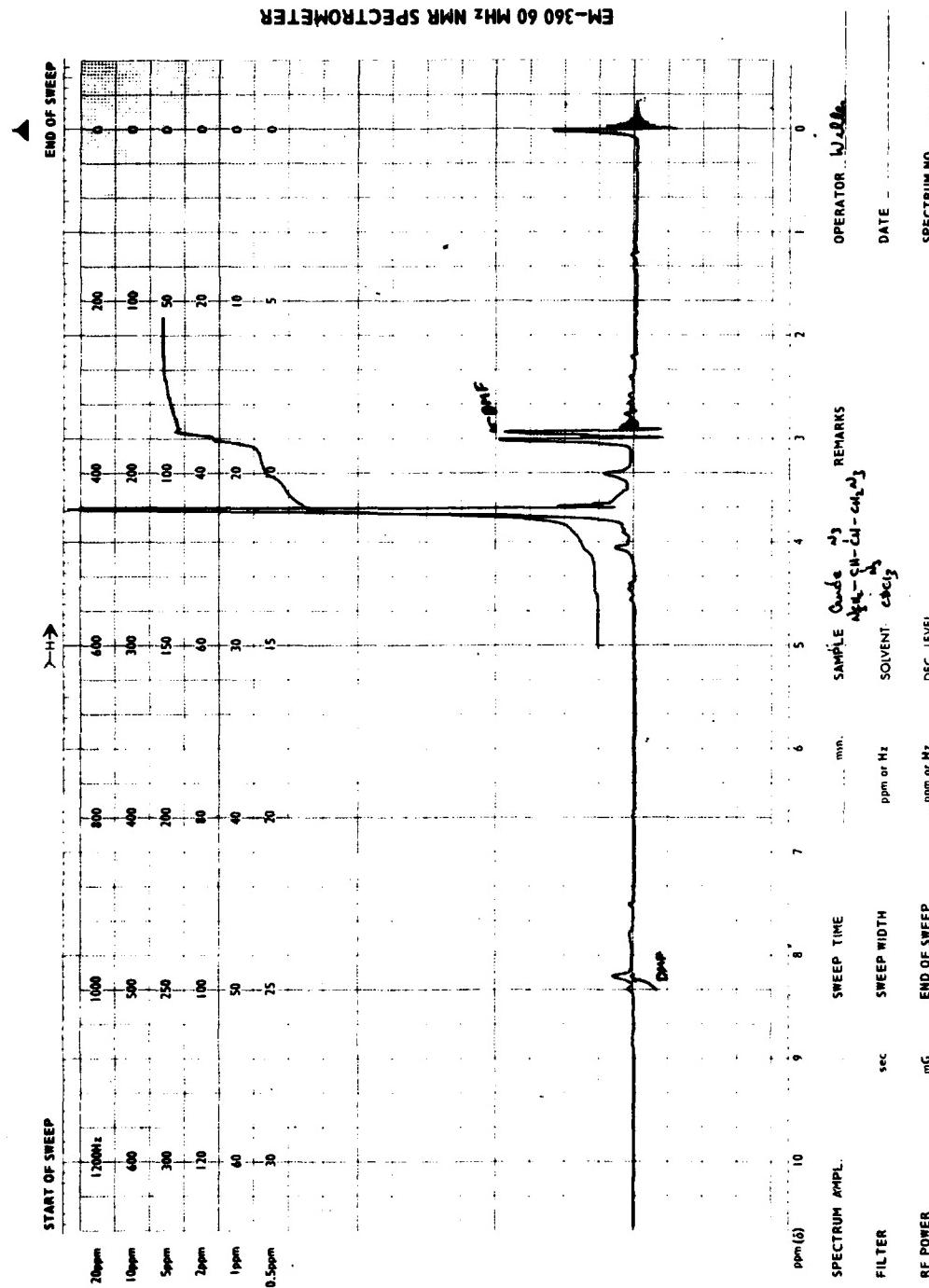


FIGURE B-5. NMR Spectrum of *Threo*-1,2,3,4-tetraazidobutane (19).

NWC TP 6416

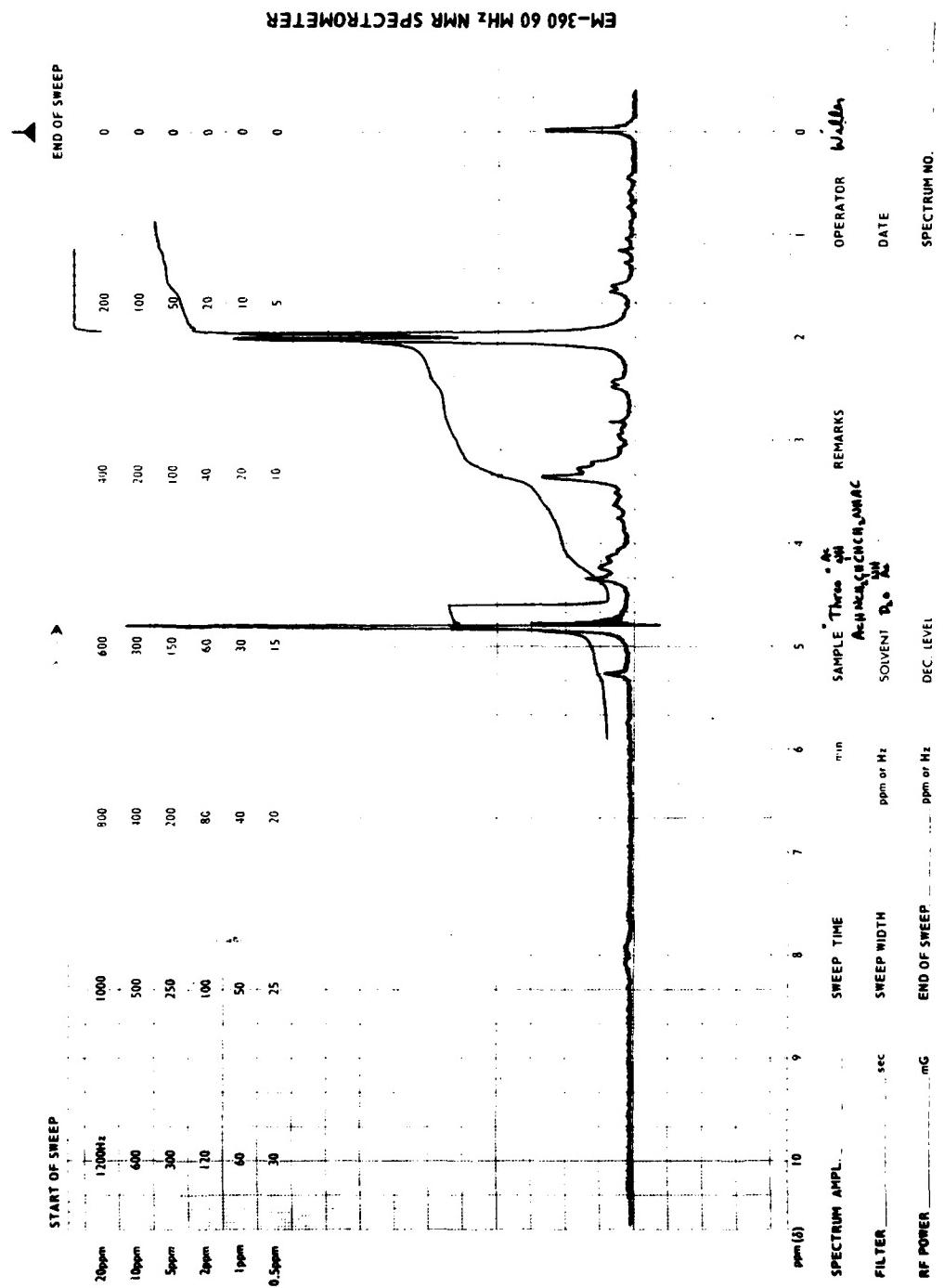


FIGURE B-6. NMR Spectrum of Threo-1,2,3,4-tetraacetamidoobutane (10b).

NWC TP 6416

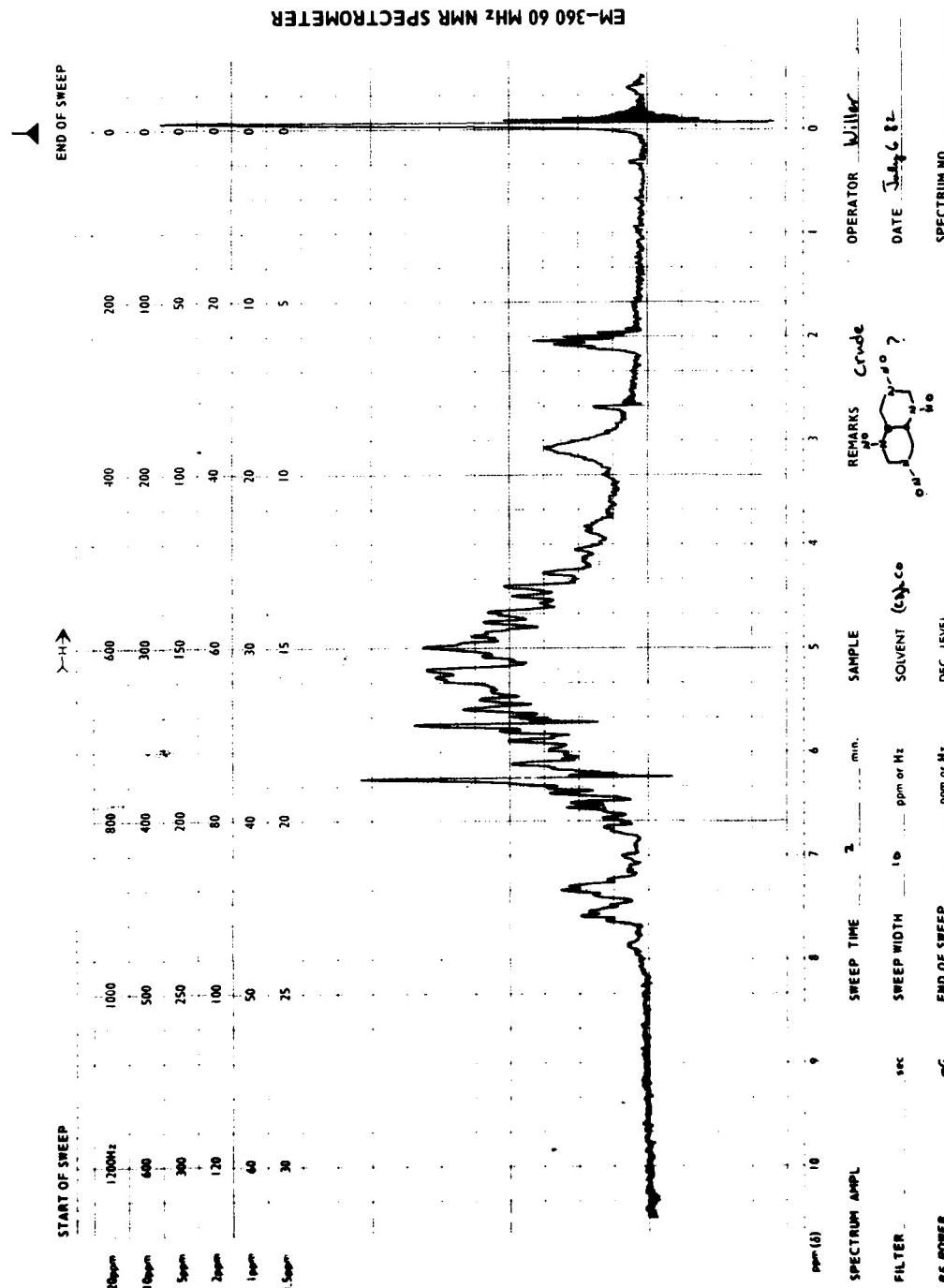


FIGURE B-7. NMR Spectrum of a Mixture of (*t*-*s*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (8) and *D*-(4,4')-bi-(1,3-dinitroso-1,3-diazacyclopentane) (22).

NWC TP 6416

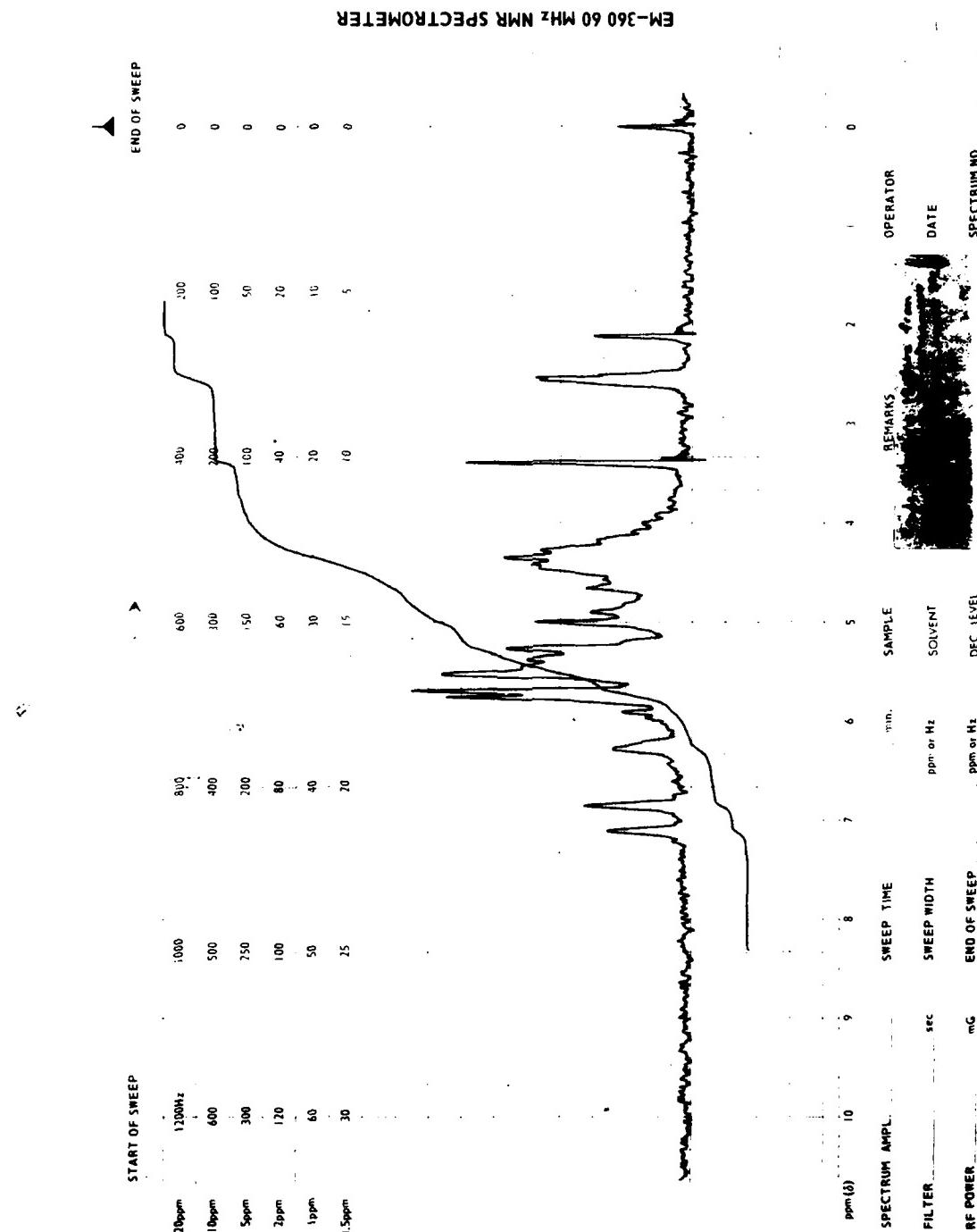


FIGURE B-8. NMR Spectrum of the Crude Product From the Nitrolysis of a Mixture of *Cis*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (8) and *D*-(4,4')-bi-(1,3-dinitroso-1,3-diazacyclopentane) (22) which is Rich in γ -4,4'-*(1,3-dinitro-1,3-diazacyclo-
 γ -pentane) (3).*

NWC TP 6416

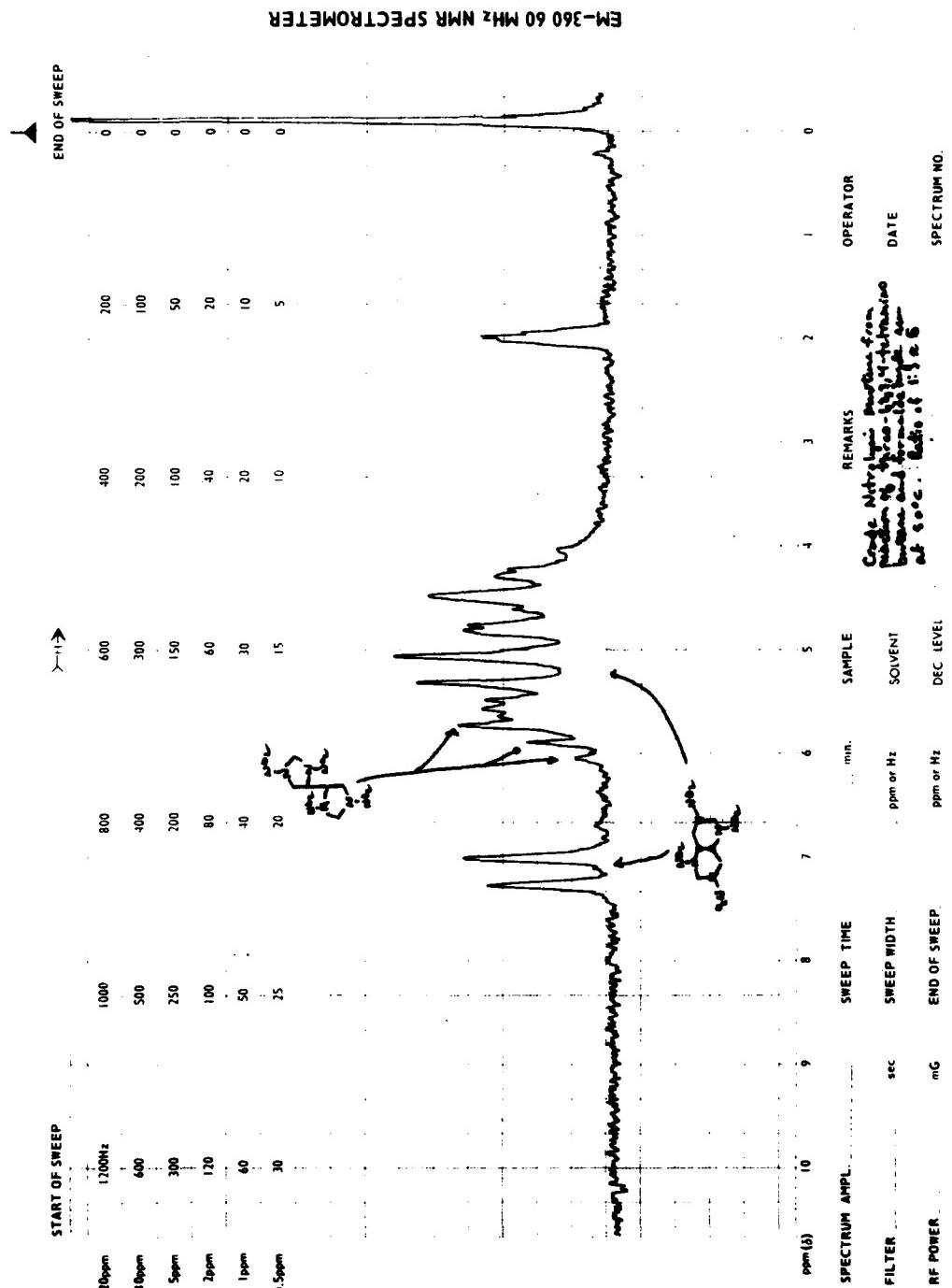


FIGURE B-9. NMR Spectrum of the Crude Product From the Nitrolysis of a Mixture of *Cis*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (8) and *D*-(4,4')-bi-(1,3-dinitroso-1,3-diazacyclopentane) (22) Which is Rich in *cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (1).

NWC TP 6416

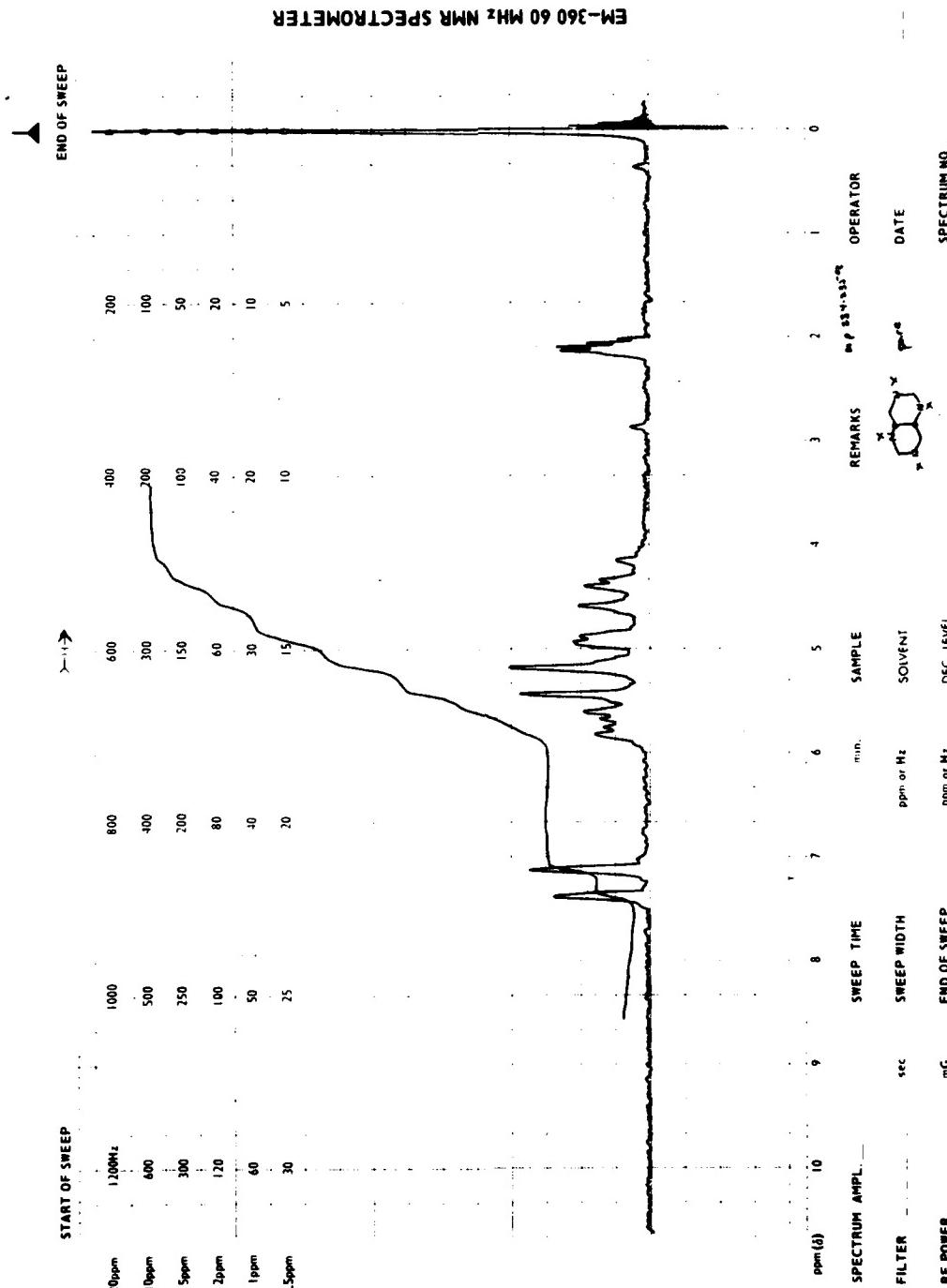


FIGURE B-10. NMR Spectrum of *Cis*-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (*L*).

NWC TP 6416



FIGURE B-11. NMR Spectrum of *D*-4,4'-(1,3-dinitro-1,3-diazacyclopentane) (3).

NWC TP 6416

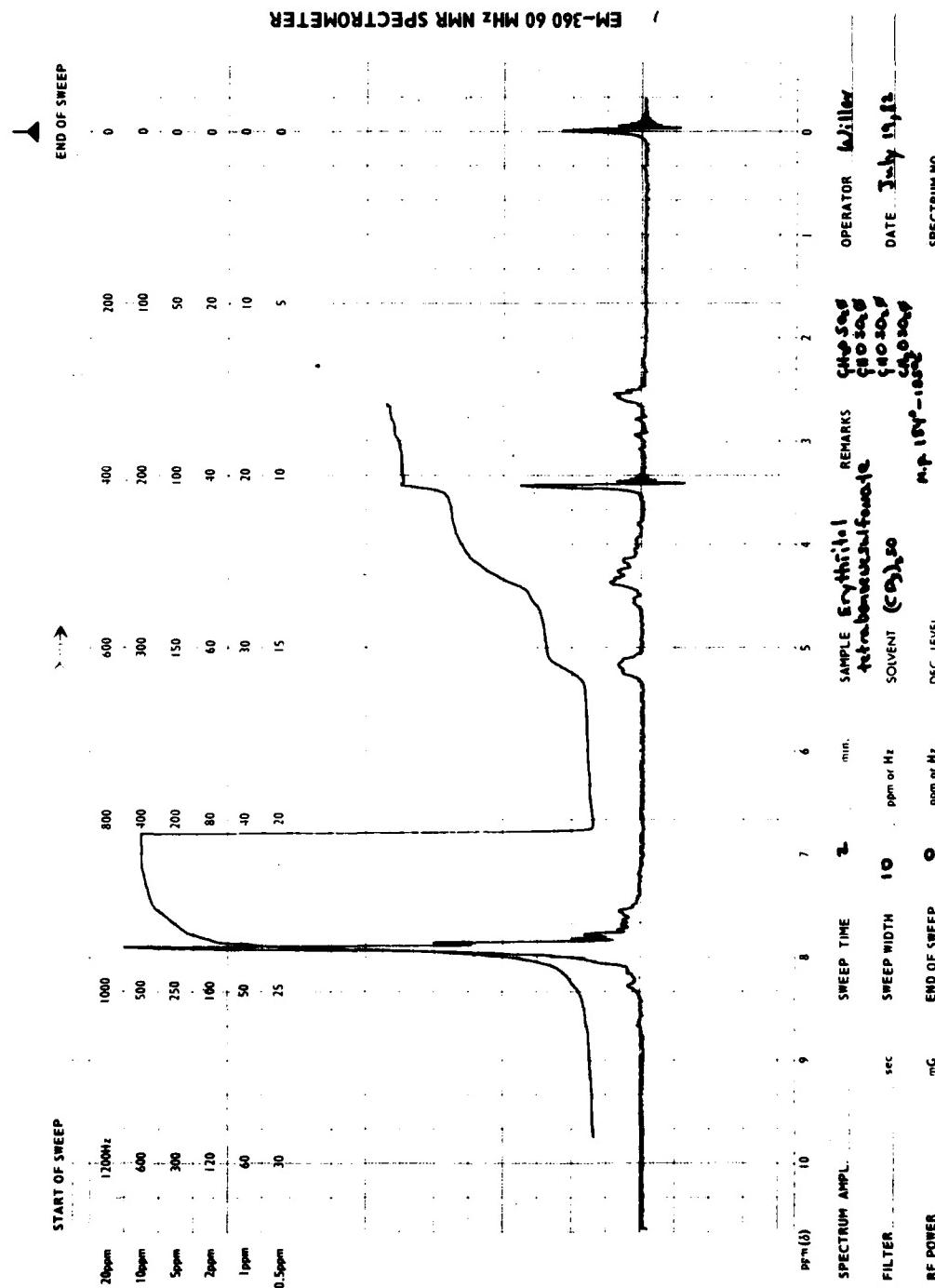
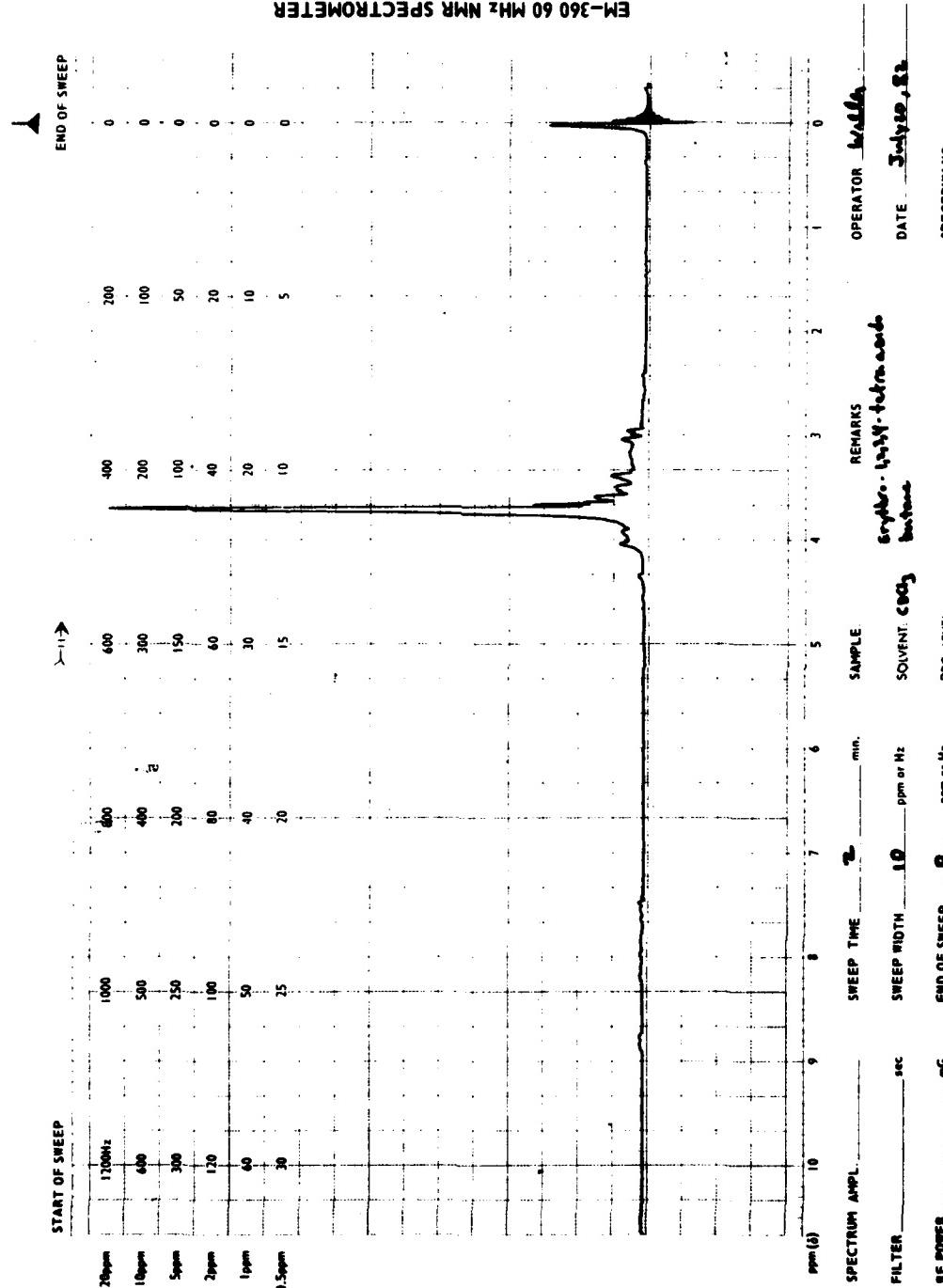


FIGURE B-12. NMR Spectrum of Mesomerized Erythritol Tetrabenzenesulfonate (23).

NWC TP 6416

EM-360 60 MHz NMR SPECTROMETER



NWC TP 6416

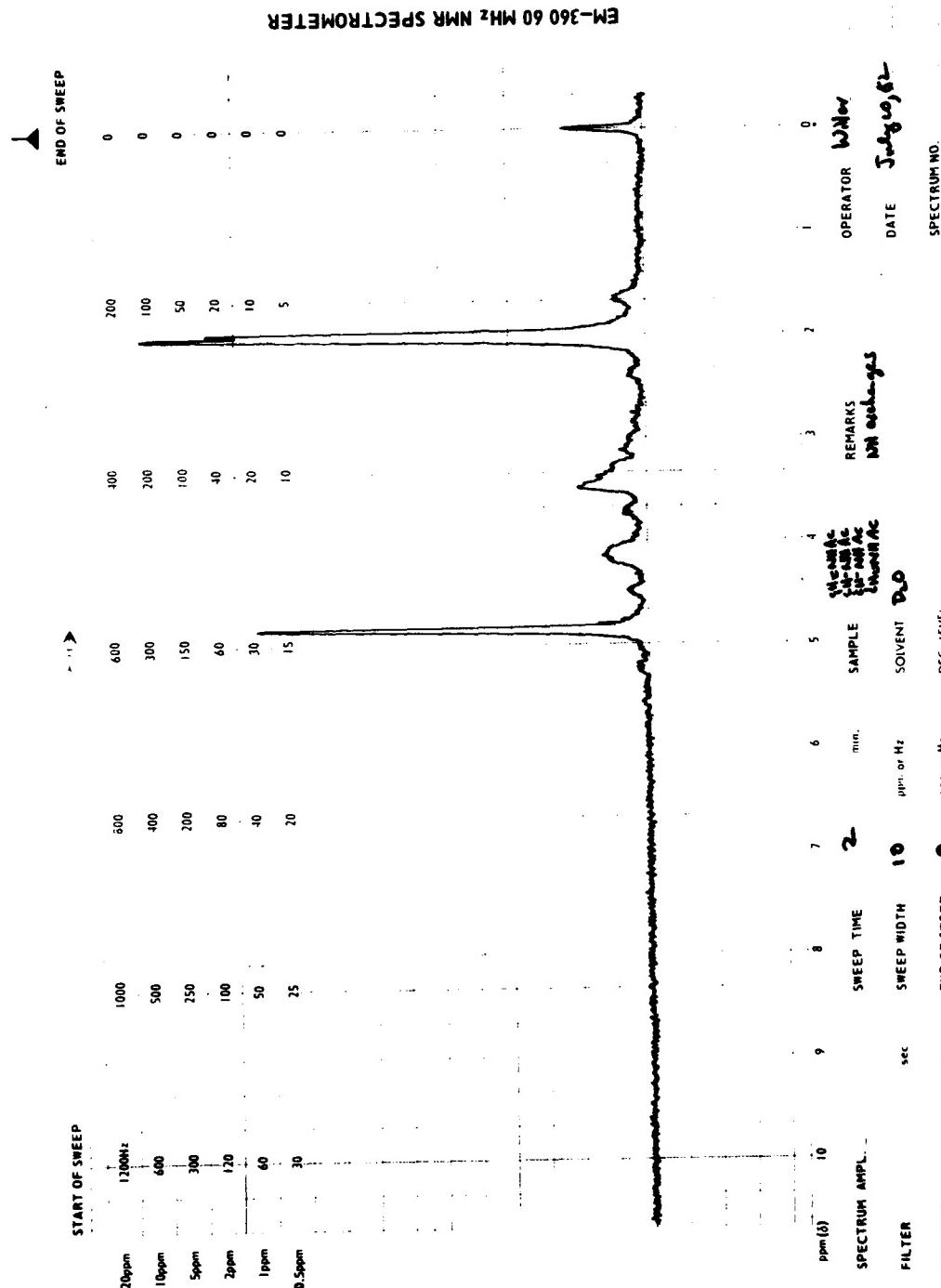


FIGURE B-14. NMR Spectrum of *M*-SO-1,2,3,4-tetraacetamiddobutane (13b).

NWC TP 6416

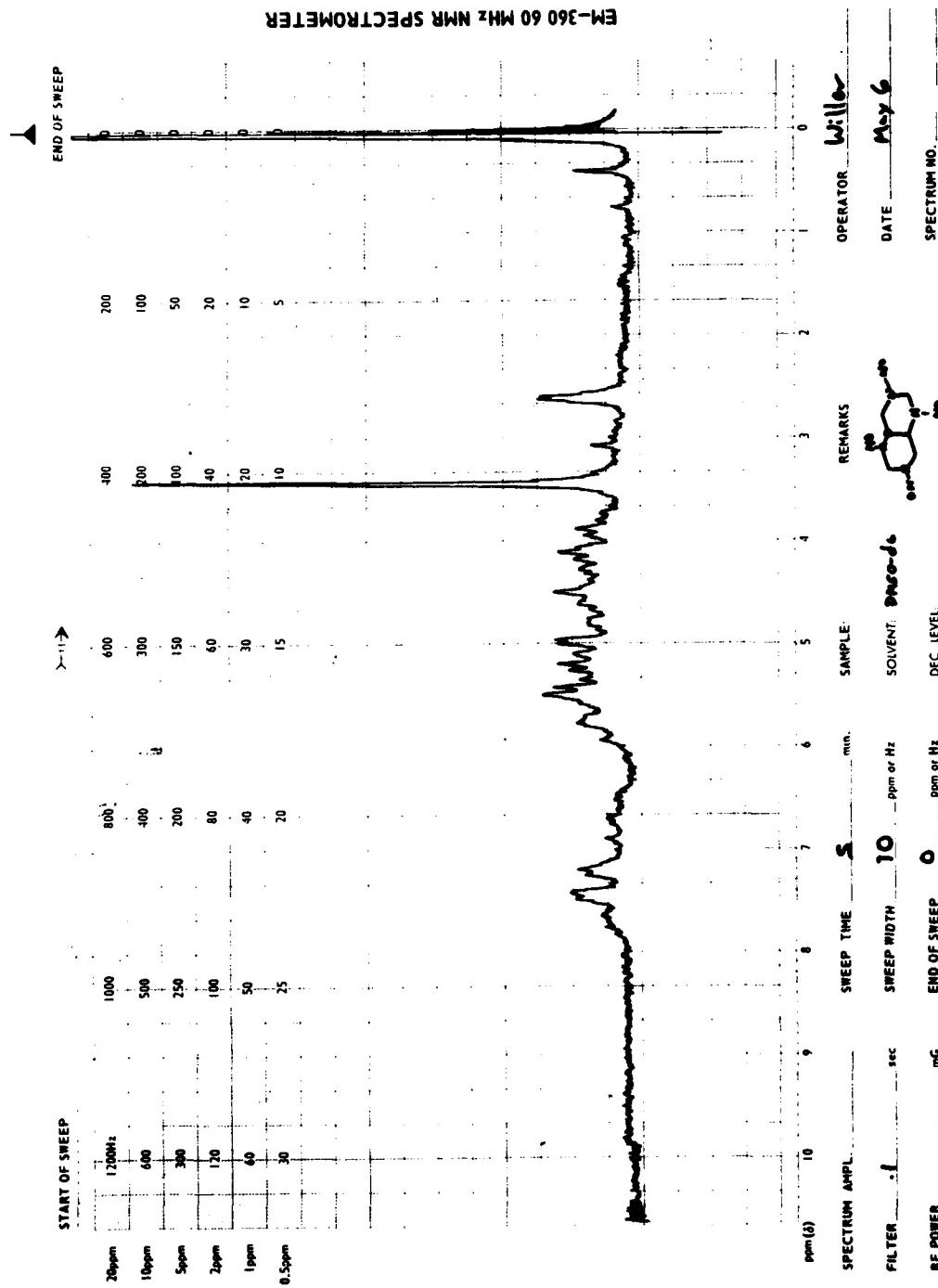


FIGURE B-15. NMR Spectrum of *Trans*-1,3,5,7-tetranitroso-1,3,5,7-tetraazadecalin (11).

NWC TP 6416

EM-360 60 MHz NMR SPECTROMETER

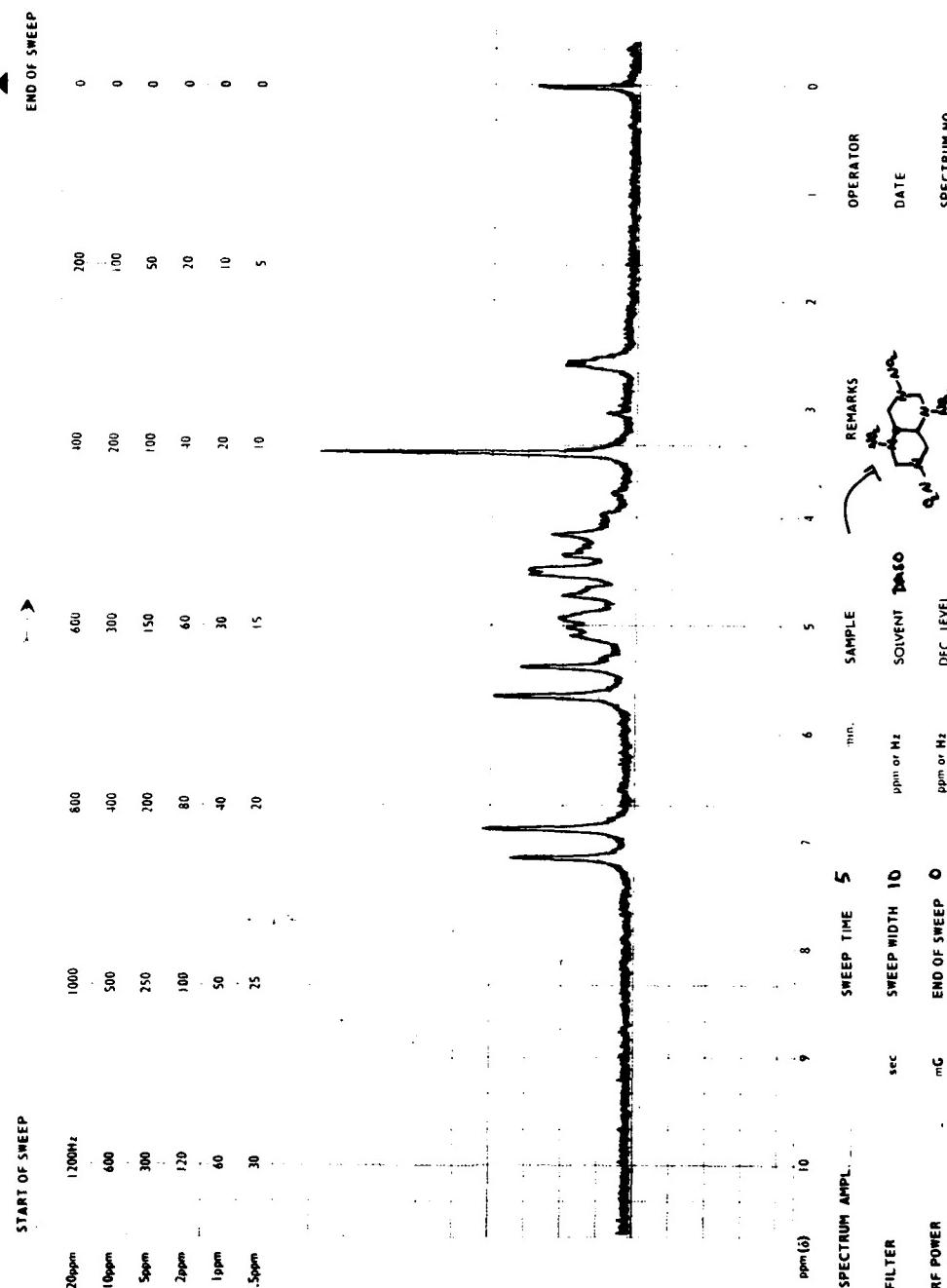


FIGURE B-16. NMR Spectrum of *Trivivil-1,3,5,7-tetranitro-1,3,5,7-tetraazadecalin (2)*.

NWC TP 6416

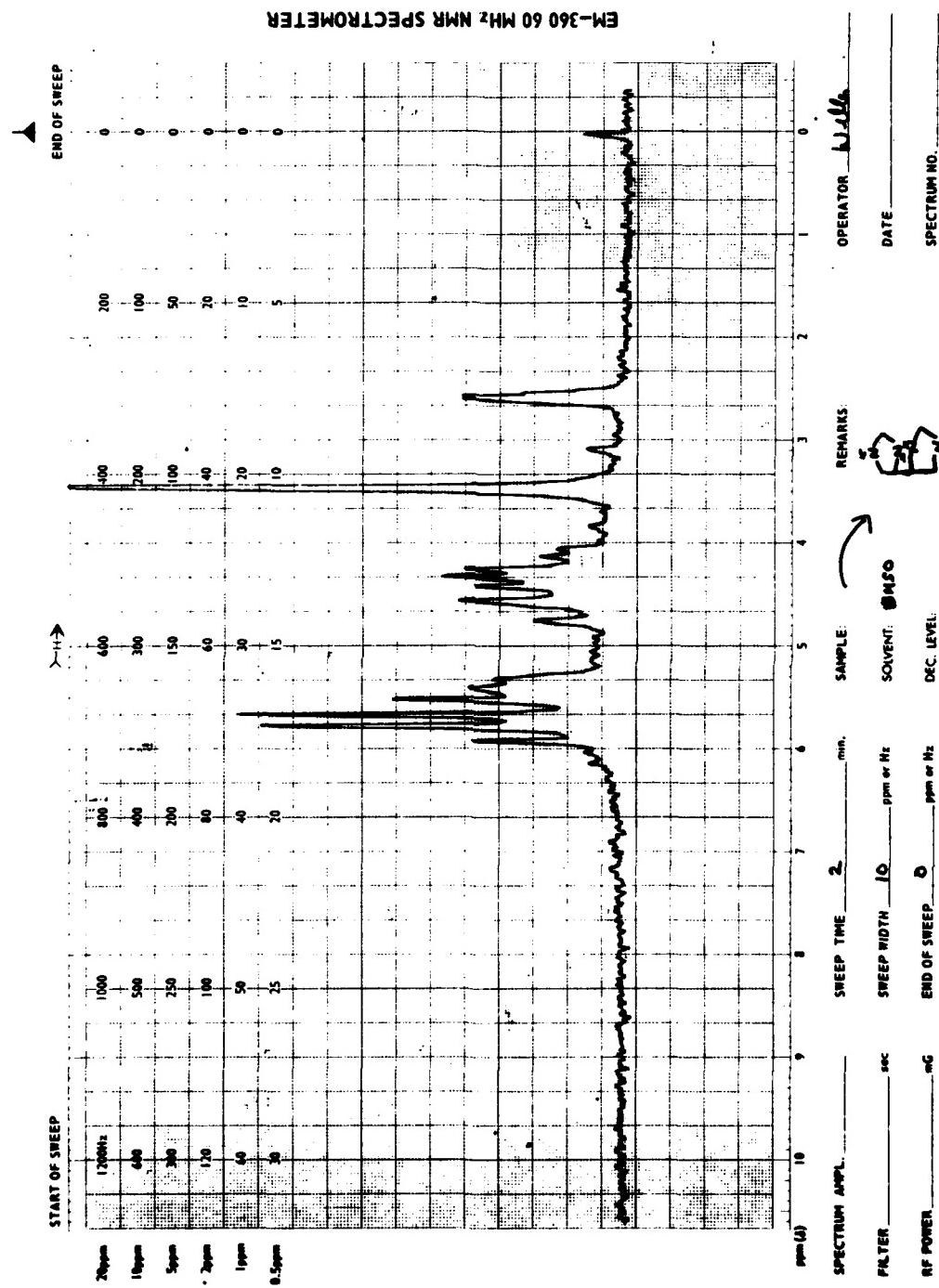


FIGURE B-17. NMR Spectrum of *Meso*-4,4'-(1,3-dinitro-1,3-diaza-cyclopentane) (4).

INITIAL DISTRIBUTION

11 Naval Air Systems Command

AIR-00D4 (2)

AIR-31 (1)

AIR-32 (1)

AIR-32R (1)

AIR-330 (1)

AIR-350 (1)

AIR-541 (1)

AIR-5411 (1)

AIR-5413 (1)

AIR-6301 (1)

5 Chief of Naval Operations

OP-225 (1)

OP-354 (1)

OP-506 (1)

OP-982E (1)

OP-982F (1)

1 Chief of Naval Research, Arlington (ONR-413, R. Miller)

5 Naval Sea Systems Command

SEA-62R (3)

SEA-99612 (2)

1 Commander in Chief, U.S. Pacific Fleet (Code 325)

1 Commander, Third Fleet, Pearl Harbor

1 Commander, Seventh Fleet, San Francisco

1 Naval Academy, Annapolis (Environmental Sciences Department, J. Williams, Assistant Chairman)

2 Naval Ordnance Station, Indian Head

Code F581, K. Wagaman (1)

Technical Library (1)

3 Naval Ship Weapon Systems Engineering Station, Port Hueneme

Code 5711, Repository (2)

Code 5712 (1)

6 Naval Surface Weapons Center, Dahlgren

R10 (1)

R11

H. Adolph (1)

K. Mueller (1)

R12

F. Menz (1)

L. Roslund (1)

Technical Library (1)

1 Naval War College, Newport

1 Naval Weapons Station, Yorktown (NEDED)

1 Office of Naval Technology, Arlington (MAT-0716, A. J. Faulstich)

3 Army Armament Research and Development Command, Dover

DRDAR-LCE (1)

DRDAR-LCE-C, Chemistry Branch (1)

DRDAR-LCU-E (1)

NWC TP 6416

- 4 Army Ballistic Research Laboratory, Aberdeen Proving Ground
 - DRDAR-BI.P, Watermeier (1)
 - DRDAR-BI.T, Dr. P. Howe (2)
 - DRDAR-TSB-S (STINFO) (1)
- 3 Air Force Systems Command, Andrews Air Force Base
 - AFSC/DLFP (1)
 - AFSC/DLWA (1)
 - AFSC/SDZ (1)
- 3 Air Force Armament Laboratory, Eglin Air Force Base
 - AFATL/DLDE (1)
 - AFATL/DLJW (1)
 - AFATL/DLODL (1)
- 12 Defense Technical Information Center
- 1 Department of Defense Explosives Safety Board, Alexandria (6-A-145)
- 2 Johns Hopkins University, Applied Physics Laboratory, Laurel, MD
- 1 Johns Hopkins University, Applied Physics Laboratory, Chemical Propulsion Information Agency, Laurel, MD
- 1 Los Alamos National Laboratory, Los Alamos, NM (R. Rogers)
- 5 University of California, Lawrence Livermore National Laboratory, Livermore, CA
 - C. Coon (1)
 - B. Dobratz (1)
 - M. Finger (1)
 - J. Kury (1)
 - H. Rizzo (1)

END

FILMED